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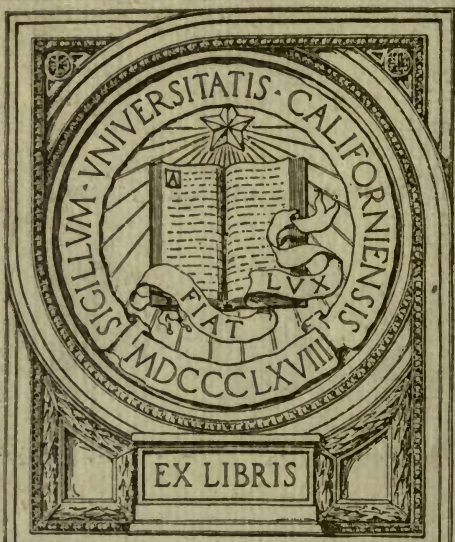

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A TREATISE ON CHEMISTRY.

A

TREATISE ON CHEMISTRY.

BY

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VOLUME II.—METALS.

PART II.

"*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723.

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PREFACE TO VOL. II.

THE aim which the Authors have set before themselves in treating of the Metals and their Compounds is the same as that which they proposed in the discussion of the Non-Metallic Elements. Owing, however, to the large number of the Metals and their Salts, the description of these latter could not, within practicable limits, be made so complete as is possible in the case of the Non-Metallic Compounds. Hence the Authors, whilst giving the characteristic properties of each metal, have been obliged to restrict their notice to those compounds which possess the greatest interest either of a theoretical or practical kind.

Due attention has been paid to the more important technical processes connected with Metallurgy, and no pains have been spared to assist the description of such processes by Drawings of the most modern forms of apparatus and plant.

As an illustration of this the Authors would refer to the Chapter on the Soda and Glass Manufactures in Part I., and to the Metallurgy of Iron in Part II.

At the end of the volume will be found short Chapters on the Classification of the Elements; on Spectrum Analysis, so far as the detection of terrestrial matter is concerned; and on the Condensation of the so-called Permanent Gases, a result which has been achieved since the publication of the First Volume.

MANCHESTER, *September* 1879.

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CHEMISTRY.

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CHEMISTRY.

VOLUME II. — PART II.

METALS OF THE IRON GROUP.

Manganese.	Cobalt.
Iron.	Nickel.

312 THE monoxides of these metals are basic oxides, whose sulphates form double salts with the sulphates of the alkali metals, and these are isomorphous with the double sulphates of the magnesium group. The metals of this group are also connected with those of the foregoing group, inasmuch as manganese and iron form sesquioxides, which act as feebly basic oxides, whilst their sulphates form alums with the sulphates of the alkali metals. The sesquioxides of nickel and cobalt, on the other hand, act as peroxides. In addition to these, certain acid-forming oxides, or their corresponding acids, are also formed by the metals of this group.

MANGANESE, Mn. = 54·8.

313 Black oxide of manganese, manganese dioxide, or pyrolusite, was known in early times, but for a long period this compound was confounded with magnetic iron ore, and this fact explains the statement of Pliny that loadstone was employed in the manufacture of glass for the purpose of removing or attracting the impurities or colouring matters out of the glass. He distinguished moreover several kinds of magnes; one of these, which is of the feminine gender, does not attract iron: "magnes qui niger est et feminei sexus, ideoque sine

viribus." This probably was manganese dioxide. The derivation of the word magnet appears to be doubtful. In the middle ages loadstone was distinguished as *magnes*, or *magnesius lapis*. Pyrolusite however was termed *magnesia* probably because Pliny had already pointed out the existence of two species of loadstone. Basil Valentine, too, as well as many later chemists, believed it to be an ore of iron. They likewise mention its use in glass-making, and in the Latin manuscripts of the sixteenth century it is designated by the term *lapis manganensis*, or similar names.

In 1740 Pott, in his treatise entitled "*Examen chymicum magnesia vitrariorum, Germanis Braunstein*," proved that the black oxide of manganese does not contain iron, and that from it a definite series of salts can be obtained. He did not, however, suggest that it contained a new metal. Scheele's celebrated investigations on manganese were published in the year 1774. In these he showed that the mineral manganese possesses a strong attraction for phlogiston, and that it takes this substance up, uniting with acids to form colourless salts; this being explained, according to our present views, by the fact that it gives off oxygen. On the other hand, the solutions of manganese which do not contain phlogiston were shown to be coloured. Scheele believed that the earth contained in this mineral resembled lime; but in the above-mentioned year Bergman, founding his deductions upon Scheele's experiments, came to the conclusion that manganese is probably the calx of a new metal, inasmuch as it colours glass, and its solutions are precipitated by prussiate of potash, these being reactions common to the metallic calces. Gahn was however the first to isolate the new metal. In Germany this was called Braunstein-könig or Braunstein-metal. In other languages, in which braunstein was termed *magnesia niger*, in order to distinguish it from *magnesia alba*, the metal was called manganese or manganesium.

Manganese chiefly occurs in nature as the dioxide or pyrolusite, MnO_2. It is also found in the following minerals: braunite, Mn_2O_3; hausmannite, Mn_3O_4; psilomelane, $(MnBa)O + MnO_2$; manganite, $Mn_2O_2(OH)_2$; rhodocrozite or manganese-spar, $MnCO_3$, which also occurs frequently as an isomorphous constituent in ferrous carbonate and other similar minerals. Manganese also occurs as alabanite or sulphide of manganese, MnS; and hauerite, or manganese disulphide, MnS_2. Manganese likewise forms an essential constituent of many other minerals, although only

occurring in them in small quantity. Thus, for instance, most silicates contain manganese, which frequently imparts to them their peculiar colour. By means of these minerals the metal manganese passes into the soil, whence it is absorbed in small quantities into the bodies of plants and animals.

314 *Preparation of Metallic Manganese.* The higher oxides of manganese are reduced to manganese monoxide when they are heated to redness, the metal not being formed either when the oxide is heated alone or mixed with charcoal in a current of hydrogen, until the temperature rises to a white-heat. The original method of preparing the metal, proposed by John,[1] depends upon this fact. Finely-divided oxide of manganese, obtained by the calcination of the carbonate in a covered crucible, is well mixed with carbon, and the mixture formed into a paste with oil; the paste is then introduced into a crucible lined with charcoal, and the upper portion completely filled with powdered charcoal. The crucible is first heated to redness for half-an-hour to solidify the mass, after which the cover is carefully luted down, and the whole exposed in a wind furnace for an hour-and-a-half to the highest temperature which the crucible can support without fusing. The regulus thus prepared contains both carbon and silicon derived from the ashes of the wood charcoal. By igniting the metal a second time in a charcoal crucible with some borax it was obtained by John in a more fusible and brilliant state, and so free from carbon that it left no black residue when treated with an acid.

Deville's[2] method consists in mixing red manganese oxide, Mn_3O_4, prepared by heating the artificial dioxide, with sugar charcoal insufficient in quantity for complete reduction. The mixture is placed in a doubly-lined crucible and heated to whiteness. The regulus obtained is coated with a violet crystalline mass which appears to be calcium-manganese spinelle, CaO,MnO_3.

Hugo Tamm,[3] who has made a number of experiments on the preparation of the metal on the large scale, suggests the following as the best method of preparation. A flux is prepared of twenty parts of powdered soda-lime glass and seven parts of fluor-spar; six parts of this mixture are then added to one part of lampblack and eleven parts of powdered black oxide of manganese. The mass is heated in a plumbago crucible which has been lined with a mixture of three parts of graphite and one part of fire-clay, and this is then intensely ignited in a wind

[1] Gehlen's *Journ. Chem. Phys.* iii. 452.
[2] *Ann. Chim. Phys.* [3], xlvi. 182.
[3] *Chem. News*, 1872, 111.

furnace. A green slag termed "green flux" is obtained in this operation, together with metallic manganese, and this flux serves for a fresh operation. Seven parts of this flux are mixed with ten parts of the best manganese dioxide, one part of lampblack, and some oil. The mass is brought into a similar crucible, covered with a thick piece of wood, and the cover luted down, a small opening being left for the escape of the gases which are evolved. It is first heated gently and then ignited at a white-heat for several hours. In this way four parts of impure manganese metal are obtained, which is found to be covered with a grey slag which may be employed for further melting operations, especially if some of the first flux be added.

This impure manganese, termed cast-manganese, contains a variety of impurities. A specimen of pyrolusite containing 50·5 per cent. of manganese, and 3·5 per cent. of iron gave a regulus having the following composition:—

Manganese	96·90
Iron	1·05
Aluminium	0·10
Calcium	0·05
Phosphorus	0·05
Sulphur	0·05
Silicon	0·85
Carbon	0·95
	100·00

After fusion with half its weight of manganese carbonate the above regulus yielded a product possessing the following composition:—

Manganese	99·910
Iron	0·050
Silicon	0·015
Carbon	0·025
	100·000

Jordan[1] describes a method of preparing metallic manganese on a large scale by treating manganese ores in a blast furnace. The metal obtained is cast-manganese, containing eighty-five per cent. of manganese, six per cent. of carbon, eight per cent. of iron, and traces of silicon, sulphur, and phosphorus.

[1] *Comptes Rendus*, lxxxvi. 1374.

Another process of preparing the metal, proposed by Brunner,[1] consists in igniting a mixture of fluor-spar and chloride of manganese with metallic sodium. The metal may also be obtained by the electrolysis of a concentrated solution of the chloride according to the process described by Bunsen.[2]

Properties. Pure manganese, obtained by the reduction process, is a grey or reddish-white metal, having the colour and appearance of cast-iron. It is very hard and brittle, has a specific gravity of about 8·0, and oxidises so easily in the air that it must be kept under rock-oil or in well-sealed vessels. Cast-manganese containing iron is however unalterable in the air. Manganese is extremely soluble in all dilute acids, and decomposes in warm water with evolution of hydrogen. It melts at a white heat.

Alloys of Manganese.

The alloys of manganese and copper closely resemble those of tin and copper.[3] Those which contain from five to eight per cent. of manganese are malleable, but those in which a higher percentage of manganese is present become grey and brittle. Alloys of manganese, copper, and zinc closely resemble German silver, and may serve as a substitute for this substance.[4] They are obtained by melting mixtures of the oxides with carbon.

MANGANESE AND OXYGEN.

315 Manganese forms a series of oxides, of which the following are the best defined:—

Manganese monoxide, MnO.
Red manganese oxide, Mn_3O_4.
Manganese sesquioxide, Mn_2O_3.
Manganese dioxide or peroxide, MnO_2.
Manganese heptoxide, Mn_2O_7.

The first of these is a powerful basic oxide; the last is an acid-forming oxide, yielding permanganic acid, $HMnO_4$, when brought into contact with water. The three intermediate oxides are feebly basic, and amongst these the peroxide also acts as a weak acid. In addition to these, we are acquainted with the salts of manganic acid, H_2MnO_4, but the acid itself, as well as the oxide corresponding to it, has not been isolated.

[1] *Pogg. Ann.* ci. 264.
[2] *Ibid.* xci. 619.
[3] Valenciennes, *Compt. Rend.* lxx. 607.
[4] Allen, *Chem. News*, xxii. 194.

MANGANOUS COMPOUNDS.

316 *Manganous Oxide,* or *Manganese Monoxide,* MnO, is best prepared by fusing together a mixture of equal parts of anhydrous manganese chloride and sodium carbonate, to which some sal-ammoniac has been added, and lixiviating the fused mass with water.[1] It is also obtained when a higher oxide or the carbonate is ignited in a current of hydrogen. Manganous oxide is a greyish-green powder, which fuses at a white-heat without loss of oxygen. It has a specific gravity of 5·09. When the powdered oxide is heated in an atmosphere of hydrogen containing a very small quantity of hydrochloric acid, it is obtained crystallised in transparent regular octohedrons of an emerald-green colour and an adamantine lustre.[2]

Manganous Hydrate, $Mn(OH)_2$, is obtained as a white precipitate when caustic alkali is added to the solution of a manganese salt. As it oxidises rapidly in the air, assuming a brown colour, it must be precipitated in an atmosphere free from oxygen, and dried at a moderate heat in a current of hydrogen gas. The powder thus obtained is frequently pyrophoric, and when touched with a piece of red-hot charcoal it begins to glow at the point of contact, the oxidation proceeding rapidly throughout the mass.

Manganous Chloride, $MnCl_2$, is formed when the metal is burnt in chlorine gas, or when hydrochloric acid is passed over heated manganous carbonate. Prepared in this way manganese chloride is a pale rose-coloured mass, having a lamino-crystalline structure. When heated to redness it fuses to an oily liquid, and decomposes in moist air with formation of hydrochloric acid and the oxides of manganese. Manganese chloride is obtained in solution by dissolving the carbonate or any of the oxides in hydrochloric acid. For this purpose the residues from the preparation of chlorine by means of pyrolusite and hydrochloric acid may be utilised. These are always coloured yellow, from the presence of ferric chloride, and contain an excess of acid. They must be evaporated to drive off the acid, then diluted with water, and a quarter of the solution precipitated with sodium carbonate. The precipitate,

[1] Liebig and Wöhler, *Pogg. Ann.* xxi. 584.
[2] Deville, *Compt. Rend.* liii. 199.

which consists of manganese carbonate and ferric hydrate, is then well washed with hot water and boiled with the remainder of the liquid. By this means the whole of the iron is precipitated as ferric oxide, and in order to ascertain that the precipitation of the iron is complete, a small portion of the liquid is filtered off and a drop or two of ferrocyanide of potassium added; if free from iron only a white precipitate will be formed; if, however, the precipitate has a bluish colour, iron is still contained in solution, and the liquid requires to be boiled for a longer time with manganese carbonate. The filtrate may contain copper, barium, and calcium. The first of these metals is removed by passing a current of sulphuretted hydrogen through the liquid. If the latter two metals are present the manganese is best precipitated by sulphide of ammonium, the precipitate well washed with hot water, and then dissolved in hydrochloric acid. On evaporation, the concentrated solution deposits between 15° and 20° light pink-coloured monoclinic crystals of the hydrated chloride $MnCl_2 + 4H_2O$. According to Marignac[1] crystals are sometimes obtained of the same composition at a lower temperature; these also belong to the monoclinic system but are of a different form, being isomorphous with those of hydrated ferrous chloride, $FeCl_2 + 4H_2O$. The crystals lose two molecules of water when placed over sulphuric acid (Graham), and when heated they fuse at 87°·5 to a clear liquid. One hundred parts of water dissolves according to Brandes:

At	10°	31°	62°·5
$MnCl_2 + 4H_2O$	150	270	625 parts.

The solubility does not increase above 62°·5, the concentrated pink solution is syrupy, and the solution boils at 106°. This salt is also soluble in alcohol with a green colour, and the alcoholic solution burns on ignition with a red flame. Manganese chloride forms double salts with the chlorides of the alkali metals.

Manganous Bromide, $MnBr_2$, is obtained by heating the powdered metal in bromine vapour, and when the compound is fused it is obtained as a pale-red mass. When the carbonate is dissolved in hydrobromic acid the hydrated bromide, $MnBr_2 + 4H_2O$, is obtained, and this has been found by Marignac to be isomorphous with the ordinary form of the chloride.

Manganous Iodide, $MnI_2 + 4H_2O$, is obtained crystallised

[1] *Comptes Rendus*, xlv. 650.

in colourless deliquescent needles, which become coloured brown on exposure to air. By careful drying the compound may be obtained in the anhydrous state as a white crystalline mass which can be fused in absence of air and oxidises on exposure to the atmosphere with evolution of iodine vapours.

Manganous Fluoride, MnF_2, is obtained by dissolving the carbonate in hydrofluoric acid, the compound being deposited on evaporation in distinct amethyst-coloured crystals, which are insoluble in pure water, but dissolve in water containing free hydrofluoric acid.

317 *Manganous Sulphate,* $MnSO_4$, is best prepared by mixing commercial black oxide of manganese to a paste with sulphuric acid and heating the mixture in a crucible to strong redness when the greater part of the iron sulphate is destroyed. The filtrate obtained after lixiviating the residue is then heated with a small quantity of manganous carbonate in order to precipitate the last traces of iron. If the concentrated solution of the salt be allowed to evaporate at a temperature below 6° rhombic crystals, having the composition $MnSO_4 + 7H_2O$, are deposited, and these are isomorphous with ferrous sulphate. Between 7° and 20°, crystals are deposited having the composition $MnSO_4 + 5H_2O$, and these are isomorphous with copper sulphate (Mitscherlich, Regnault). At a temperature of from 20° to 30° transparent rose-coloured quadratic crystals or large colourless prisms, having the composition $MnSO_4 + 4H_2O$, are deposited, which possess a specific gravity of 2·092 (Kopp); at the same time a crystalline crust of a salt having the composition $MnSO_4 + 3H_2O$ is formed. When these hydrates are heated to 200°, or when a concentrated aqueous solution is boiled, the anhydrous salt, $MnSO_4$, is deposited as a reddish-yellow powder (Graham), which becomes colourless at a higher temperature. It possesses a specific gravity of 3·1, and is decomposed at a bright red-heat, leaving a residue of red oxide of manganese. A solution saturated at 6° contains 36 per cent. of the anhydrous salt, and boils at 102°. The salt containing four molecules of water is more soluble in cold than in boiling water, and when its concentrated solution is heated, a crystalline crust separates out, and this on cooling again dissolves. This peculiarity depends upon the formation of the different hydrated salts. According to Brandes 100 parts of water dissolve:

At	6°	10°	75°	101°
$MnSO_4 + 4H_2O$	113	126·5	145	92·7 parts.

Manganous sulphate is insoluble in absolute alcohol, this liquid removing a portion of the water from the hydrates. Finely crystalline double sulphates are formed when manganous sulphate and the sulphates of the alkali-metals are crystallised together, and these are isomorphous with the corresponding salts formed by magnesium and by copper.

Manganous Aluminium Sulphate, $MnSO_4 + Al_2(SO_4)_3 + 24H_2O$. This substance occurs as the mineral apjohnite found in Algoa Bay in South Africa.[1]

Manganous Dithionate, $MnS_2O_6 + 3H_2O$. This salt is of interest inasmuch as it is employed for the preparation of dithionic acid (Vol. I. page 350). It is obtained by passing sulphur dioxide through water in which finely-divided manganese dioxide is suspended. The solution always contains a small quantity of manganese sulphate, and for this reason baryta water is added as long as a precipitate is formed. Manganese dithionate is deposited in easily soluble rhombohedral crystals.

Manganous Nitrate, $Mn(NO_3)_2 + 6H_2O$, crystallises with difficulty in white deliquescent needles which readily dissolve in alcohol. The salt melts on heating, and the liquid boils at 129°·5, at which temperature a black deposit of manganese oxide is formed.

318 *Manganous Phosphates.* These salts have been investigated by Heintz,[2] Debray,[3] Bödecker,[4] and Erlenmeyer.[5] The normal manganous orthophosphate, $Mn_3(PO_4)_2 + 7H_2O$, is a white imperfectly crystalline precipitate. The monohydrogen salt, $HMnPO_4 + 3H_2O$, forms small prismatic rose-coloured rhombic crystals slightly soluble in water, and the dihydrogen phosphate, $H_4Mn(PO_4)_2 + 2H_2O$, crystallises in red four-sided prisms which deliquesce on exposure to the air, decomposing into free phosphoric acid and the preceding salt.

Manganous Arsenate. When arsenic acid is saturated with manganese carbonate, a difficultly soluble salt having the composition $HMnAsO_4$ is formed. This dissolves readily in arsenic acid with formation of the salt $H_4Mn(AsO_4)_2$, which latter crystallises in rectangular plates.

Manganous Silicates frequently occur as isomorphous constituents of many minerals. Some naturally occurring manganese silicates are known. Thus, for instance, rhodonite, $MnSiO_3$,

[1] *Phil. Mag.* xii. 103.
[2] *Pogg. Ann.* lxxiv. 450.
[3] *Ann. Chem. Pharm.* lxix. 208.
[4] *Ann. Chim. Phys.* [3], lxi. 433.
[5] Liebig's *Ann.* cxc. 191.

occurs in light brownish-red transparent triclinic crystals, and tephroite, Mn_2SiO_4, crystallises in the quadratic system in rose-red, brown, or grey masses, and usually occurs together with rhodonite.

Manganous Carbonate, $MnCO_3$, forms an isomorphous constituent of chalybite and dolomite, and also occurs in the pure state in the rose-red crystals of manganese spar or rhodochrozite. All these minerals crystallise, like calc-spar, in rhombohedrons, but manganocalcite, $(MnCaMg)CO_3$, is isomorphous with arragonite.

The hydrated manganese carbonate is obtained as a white precipitate by mixing a solution of the chloride or sulphate of manganese with carbonate of soda. In the moist state it soon becomes brown coloured on exposure to the air; it dissolves in 8,000 parts of pure water, and readily in water containing carbonic acid.

319 *Manganese and Cyanogen.* When a concentrated solution of acetate of manganese is warmed with solid potassium cyanide, a green precipitate is thrown down of $KCN,Mn(CN)_2$; this gradually disappears, and in its place dark blue crystals of potassium mangano-cyanide, $K_4Mn(CN)_6 + 3H_2O$, are formed.[1] The mangano-cyanide is also obtained when manganous carbonate is heated to a temperature of from 40° to 50° with a solution of cyanide of potassium.[2] The salt crystallises in deep violet-blue quadratic efflorescent tables. Its solution oxidises on exposure to air with formation of potassium mangani-cyanide, $K_6Mn_2(C_3N_3)_4$, which crystallises in dark-red prisms. This latter salt when brought into contact with potassium amalgam in aqueous solution is again transformed into mangano-cyanide. The constitution of these compounds, which are not double salts, will be referred to under the corresponding iron compounds.

MANGANIC COMPOUNDS.

320 *Mangano-Manganic Oxide* or *Red Oxide of Manganese*, Mn_3O_4, occurs with other manganese ores, and also by itself as the mineral hausmannite. This mineral crystallises in acute quadratic pyramids, and one of its best localities is Ilmenau in Thuringia. Its specific gravity is 4·85. If manganese monoxide

[1] Eaton and Fittig, *Ann. Chem. Pharm.* cxlv. 157.
[2] Decamps, *Bull. Soc. Chim.* [2], ix. 443.

be heated in contact with air, or if the higher oxides be heated either in contact or out of contact with air, this same compound is obtained in the form of a brownish-red powder, which then has a specific gravity of 4·72, and is converted into crystals of hausmannite by gently heating it in a slow current of hydrochloric acid.[1] It is also obtained in the crystalline form by heating a mixture of sulphate of manganese and potassium sulphate to bright redness,[2] or by treating a mixture of manganous oxide and calcium chloride in the same way.[3] This oxide dissolves in cold concentrated sulphuric acid, giving rise to a red solution containing a mixture of manganous and manganic sulphates. Hence the red oxide is considered to be a compound of $MnO + Mn_2O_3$. In other respects, however, it behaves in a similar way to the red oxide of lead. Thus on heating with dilute sulphuric acid manganous sulphate and manganese dioxide are formed, and boiling nitric acid decomposes it in a manner similar to that in which it acts on red lead:

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

Chlorine gas is given off when this oxide is heated with hydrochloric acid and manganous chloride is formed:

$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2.$$

Manganic Oxide or *Manganese Sesquioxide*, Mn_2O_3. This oxide occurs as the mineral braunite crystallised in obtuse quadratic pyramids. It possesses a sub-metallic lustre, has a dark brownish-black colour, and a specific gravity of 4·75. It may be obtained artificially by igniting any of the oxides of manganese in oxygen, or in a mixture of this gas and nitrogen, which does not contain more than twenty-six per cent. of oxygen.[4] It then forms a black powder, having a specific gravity of 4·32.

Manganic Hydroxide, $Mn_2O_2(OH)_2$, occurs in nature as manganite in steel-grey or arsenic-black crystals, belonging to the quadratic system, and having a specific gravity of 4·3. It is usually accompanied by other manganese ores, together with calcspar and heavy-spar. In general appearance it closely resembles pyrolusite (manganese dioxide), but it may be distinguished from this compound by its giving a brown instead of a black streak when rubbed on an unglazed porcelain plate. Manganic hydroxide is formed when manganous hydroxide is allowed to oxidise in

[1] Deville, *Compt. Rend.* liii. 199.
[2] Debray, *ibid.* lii. 985.
[3] Kuhlmann, *ibid.* lii. 1283.
[4] Dittmar, *Chem. Soc. Journ.* xvii. 294.

moist air. It forms a dark-brown powder capable of soiling very strongly, and gives off its water at a temperature above 100°. It dissolves in hot nitric acid with formation of manganous nitrate and manganese dioxide:

$$Mn_2O_2(OH)_2 + 2HNO_3 = Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

From this reaction it would appear that in constitution this body resembles lead dioxide and analogous compounds, but in other reactions it acts as a feebly basic oxide, whose salts, with a few exceptions, are very unstable.

321 *Manganic Chloride*, Mn_2Cl_6, is not known in the solid state; it can, however, be obtained in solution as a brown liquid by carefully adding the oxide or hydroxide in small quantity to cold hydrochloric acid. On heating the solution chlorine is evolved and the manganic chloride decomposed:

$$Mn_2Cl_6 = 2MnCl_2 + Cl_2.$$

Manganic Sulphate, $Mn_2(SO_4)_3$. Manganic oxide and hydroxide dissolve with difficulty in sulphuric acid. The red oxide, Mn_3O_4, on the other hand, dissolves readily, yielding a purple-red-coloured solution. If the finely-divided precipitated dioxide be treated with sulphuric acid, oxygen is evolved, and at a temperature of 138° a green liquid is obtained from which the sulphate is precipitated as a non-crystalline powder. In order to purify this salt it is brought on to a porous porcelain plate, when the greater part of the sulphuric acid is absorbed; the residue is then washed with pure nitric acid and the salt allowed to dry in absence of air on another porous plate, and then is heated to 150°,[1] but not beyond this point, as it decomposes at 160° with evolution of oxygen. It deliquesces on exposure to air, forming a violet solution, from which, especially when in contact with water, manganic hydroxide separates.

Manganic Potassium Sulphate, or *Manganese Alum*, $K_2SO_4 + Mn_2(SO_4)_3 + 24H_2O$. This is obtained when potassium sulphate is added to a solution of the foregoing salt containing an excess of sulphuric acid. On evaporation to a syrupy consistency the above salt crystallises out in violet-coloured regular octohedrons; it is decomposed in contact with water with separation of manganic hydroxide.

Manganese Ammonium Alum, $(NH_4)_2SO_4 + Mn_2(SO_4)_3 + 24H_2O$.

[1] Carius, *Ann. Chem. Pharm.* xcviii. 53.

This salt corresponds closely to the above-mentioned potassium compound, and is obtained in a similar way.

Manganic Phosphates. Both manganic oxide and the dioxide dissolve in a concentrated solution of phosphoric acid, in the latter case with evolution of oxygen, with formation of a deep violet liquid, from which a violet-coloured crystalline mass separates out (Gmelin). This decomposes in contact with water, and manganic hydroxide is precipitated from the solution by the alkalis. On evaporating the red solution a peach-blossom coloured powder separates, consisting of manganic metaphosphate, $Mn_2(PO_3)_6 + 2H_2O$.[1]

Manganese Dioxide and the Manganites.

322 *Manganese Dioxide, Manganese Peroxide,* or *Black Oxide of Manganese,* MnO_2, is the most important ore of manganese. It occurs in rhombic crystals and in crystalline and amorphous masses, being known to the mineralogist as pyrolusite. It possesses a metallic lustre, an iron-black or dark steel-grey colour, and a black streak. It is opaque and rather brittle, and has a specific gravity of 4·82. The most celebrated localities for this mineral are Ilmenau in Thuringia, near Platten in Bohemia, near Mährisch-Trubau in Moravia, on the Lahn, and in France, Spain, and North America. It occurs in the United States, abundantly at Vermont in Massachusetts, and in Red Island Bay at San Francisco; and also in New Brunswick, Nova Scotia. It is likewise found in Devonshire. Pyrolusite seldom occurs in the pure state, being generally mixed with other manganese ores such as psilomelane, $(MnBa)O + 2MnO_2$, and manganite. It also always contains ferric oxide, silica, and traces of the oxides of cobalt and nickel.

Pure manganese dioxide is obtained artificially by a moderate ignition of the nitrate. The residue is then boiled out with nitric acid, washed well, and moderately heated (Berthier). If manganous carbonate be heated to 260° in presence of air, and then the residue treated with very dilute cold hydrochloric acid, pure manganese dioxide remains behind (Forchhammer).

It is obtained in the hydrated state by precipitating a manganese solution with an alkaline solution of an hypochlorite, or by treating manganic hydroxide with hot nitric acid.[2] The

[1] Hermann, *Pogg. Ann.* lxxiv. 303.
[2] Gorgen, *Ann. Chim. Phys.* [3], lxvi. 155.

hydroxide thus obtained, when perfectly freed from nitric acid by washing with water, is soluble in water, yielding a brown solution to which the name of manganous acid has been given. This solution turns blue litmus paper red, and does not undergo alteration on standing for many weeks, but small quantities of acid or alkali produce an instant precipitation. Manganese dioxide, like lead dioxide, possesses at the same time feebly basic and feebly acid properties.

Manganese Tetrachloride, $MnCl_4$, is not known in the pure state, as it is extremely unstable. It is prepared by passing hydrochloric acid gas into a well-cooled mixture of manganese dioxide and ether. The green solution thus obtained possesses powerful oxidising properties.

Hydrobromic and hydriodic acids act in a similar way. (Nicklès.)

Manganese Tetrafluoride, MnF_4, is obtained as a brown liquid when the dioxide is carefully added to concentrated hydrofluoric acid. The brown solution possesses strong oxidising properties. Alkalis, as well as an excess of water, precipitate the dioxide, and when potassium fluoride is added a rose-red precipitate of the compound $MnF_4 + 2KF$ falls down.

323 *The Manganites.* Manganese dioxide combines with several basic oxides to form compounds which may be considered as salts of manganous acid. *Potassium Manganite,* $K_2Mn_5O_{11}$, is obtained as a yellow precipitate when carbon dioxide is passed into a solution of potassium manganate, K_2MnO_4. *Calcium Manganite,* $CaMn_5O_{11}$, is a blackish-brown precipitate formed when a solution of manganous nitrate is poured into an excess of bleaching-powder solution.

Manganese dioxide has long been used for the preparation of colourless glass, and hence pyrolusite has been known as *savon des verriers.* Its mineralogical name, indeed, has reference to this employment of the mineral (from πῦρ, fire, and λύω to wash). It also serves for the preparation of the manganese compounds and of oxygen, but by far the largest quantity of the mineral is employed for making chlorine, used in the manufacture of bleaching-powder. As this mineral never occurs in the pure state in commerce, a rapid and accurate method of determining the value of manganese ores is of great value to the manufacturer; these methods will be described under the detection and estimation of manganese.

324 *Regeneration of Manganese Dioxide from the Chlorine Residues.* Before the year 1856, the whole of the manganese chloride obtained in the manufacture of chlorine from manganese dioxide and hydrochloric acid was allowed to run to waste. In 1821, Forchhammer [1] observed that when manganous carbonate is heated to 260° in an open vessel it is converted into dioxide. Charles Dunlop [2] applied this reaction to the regeneration of manganese dioxide from the chlorine still-liquors. The free acids which these liquors contain are first neutralised with carbonate of lime, the ferric chloride being at the same time decomposed; the clear liquor is drawn off from the deposited ferric hydrate, and again treated with carbonate of lime in closed boilers under a pressure of several atmospheres. Under these circumstances the whole of the manganous chloride is converted into the carbonate:

$$MnCl_2 + CaCO_3 = MnCO_3 + CaCl_2.$$

The precipitated carbonate is then separated by subsidence, well washed, and brought on to trays on wheels, which are placed in an oven so that the manganous carbonate is exposed to the action of a current of hot air for forty-eight hours. At the end of this time the carbonate is converted into a black powder which contains about 72 per cent. of MnO_2. In 1857 this process was adopted by Messrs. Charles Tennant & Co., at St. Rollox, and applied to the regeneration of the whole of their manganese, amounting to about 10,000 tons per annum. The process is, however, somewhat costly, and has not been adopted generally by manufacturers of bleaching powder.

A much more perfect and less troublesome process was invented by Mr. Walter Weldon, in 1867, and first practically carried out at Messrs. Gamble's works at St. Helen's, in 1868. This process, which is now universally adopted both by British and Continental manufacturers, depends upon the fact that manganous hydroxide is completely transformed into dioxide by air heated to 55° when an excess of lime is present. The solution of manganese chloride freed from iron and excess of acid by means of carbonate of lime is mixed with milk of lime in 1·6 times the quantity needed for the exact precipitation of the hydroxide. The resulting mixture, consisting of manganous hydroxide, carbonate of lime, and calcium chloride, is heated by a current of steam to 55°, and a rapid current of air is blown

[1] *Ann. Phil.* xvii. 50. [2] *Report of Patent Inventions*, March, 1856, p. 236.

through the liquor. As soon as about three-quarters of the manganous oxide has been transformed into dioxide the liquor

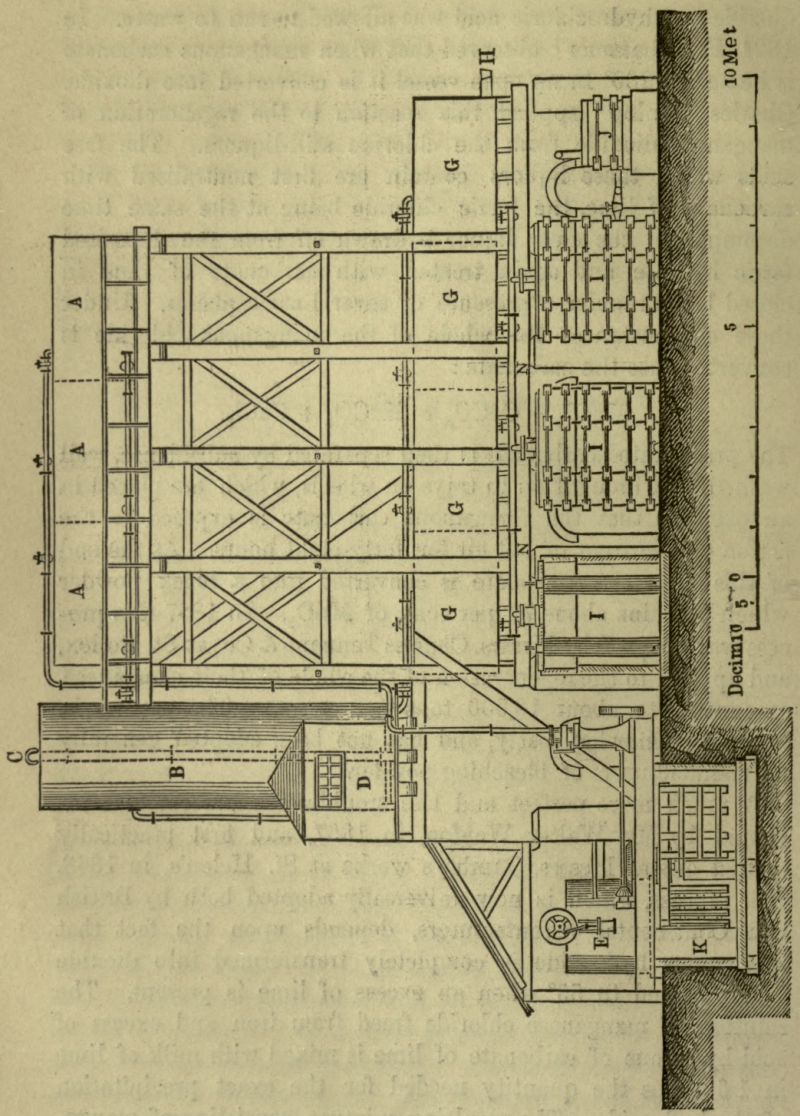

FIG. 130.

is allowed to settle, and the clear solution of calcium chloride drawn off from the deposit of black dioxide combined with lime technically termed "manganese-mud."

Fig. 130 exhibits an elevation of the most improved form of Weldon plant; Fig. 131 shows the same in plan; K is the well in which the liquor which runs from the chlorine stills I, I, I, and J, J, is neutralised with lime-stone. This liquor is then pumped up by means of the pump L into the still-liquor settlers A, A, A,

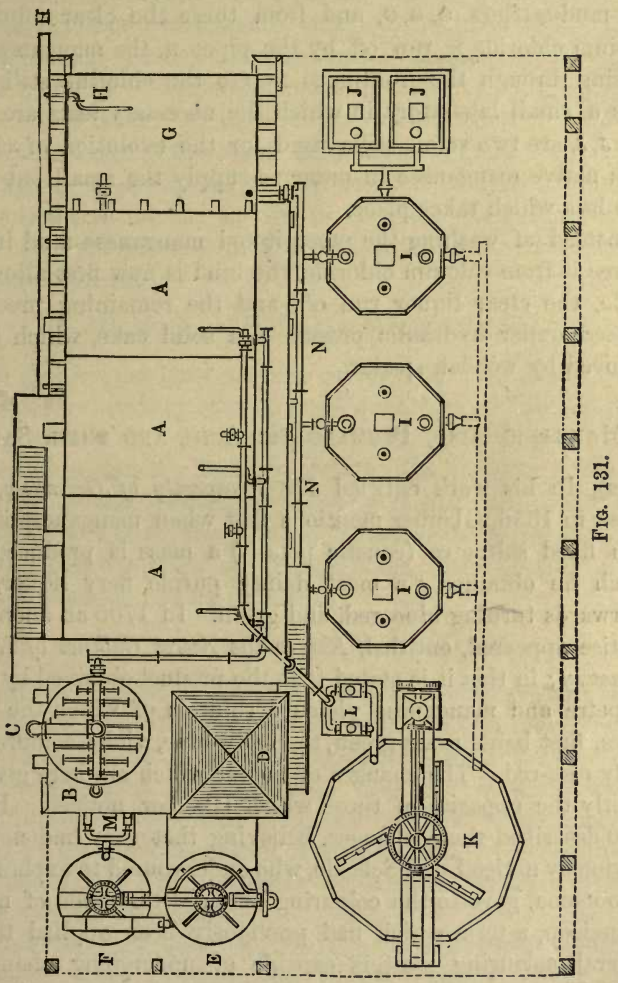

Fig. 131.

in which the oxide of iron is deposited. From the settlers the neutral chloride of manganese solution is run by means of iron pipes into the large oxidiser B; here it is mixed with milk of lime contained in the vessel F, having previously been

prepared in the vessel E, and being pumped up into the oxidiser by the pump M. Steam is then passed into the oxidiser filled with the liquor until the right temperature has been attained, and then a blast of air is blown in by means of the blowing-engines through the air-pipe C. After the operation is complete the oxidised liquor is allowed to deposit the mud in the mud-settlers G, G, G, and from these the clear solution of calcium chloride is run off by the pipes H, the manganese-mud passing through the iron pipes N into the chlorine stills, I, I, I. D is a small laboratory in which the necessary tests are made, and J, J, are two small stills used for the evolution of chlorine from native manganese in order to supply the small but inevitable loss which takes place.

Instead of washing the precipitated manganese-mud in order to free it from calcium chloride, the mud is now first allowed to settle, the clear liquor run off, and the remaining precipitate pressed under hydraulic presses to a solid cake, which is then removed by wooden spades.

Manganic Acid, Permanganic Acid, and their Salts.

325 In his work entitled *The Prosperity of Germany*,[1] published in 1656, Glauber mentions that when manganese is fused with fixed saltpetre (caustic potash) a mass is produced from which he obtained "a most dainty purple fiery liquor," this afterwards turning blue, red, and green. In 1705 an anonymous treatise appeared, entitled, *Key to the Secret Cabinet of Nature's Treasury;* in this it is stated that the product obtained by fusing saltpetre and manganese yields a solution of which the colour alters, first being grass-green, then sky-blue, violet-coloured, and lastly rose-red. The changes of colour which are here given are exactly the opposite of those which Glauber noticed. Pott in 1740 described these changes, believing that they had not been previously noticed, and Scheele, who endeavoured to explain these phenomena, gave to the colouring material the name of mineral chameleon, a term which had previously been applied to other mineral colouring matters capable of undergoing changes of tint. The properties of this mineral chameleon were afterwards investigated by many chemists, but it was not until the year 1817, when Chevillot and Edwards[2] investigated the subject, that a rational view of its composition was arrived at. They showed

[1] Packe's translation, 1689, p. 353. [2] *Ann. Chim. Phys.* [2], iv. 287.

that when much alkali is employed a green compound is formed; that when, on the other hand, an excess of manganese is fused with potash a red body is produced, and they succeeded in preparing the substance obtained by the latter reaction in the crystalline form. They also showed that an absorption of oxygen takes place, and consequently they assumed that the potash-salt forms with manganese a manganate, and that the green salt contains more base than the red. Forchhammer[1] investigated the subject in 1820, and ascribed the difference in colour to the existence of two distinct acids. It is, however, to Mitscherlich[2] that we owe a knowledge of the exact composition of these two acids.

Manganic Acid, H_2MnO_4. This acid is contained in the green solution, but it is not known in the free state, inasmuch as it at once decomposes into permanganic acid, $HMnO_4$, and manganese dioxide:

$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O.$$

The *Manganates* have a green colour, and their solutions are only stable when they contain large quantities of free alkali. If carbon dioxide be passed through them, or if they be diluted with much water, the liquid passes from a green to a blue and violet colour, the permanganate being formed, and the dioxide deposited; *vice versâ*, the permanganates are converted into manganates with evolution of oxygen, when their solution in concentrated caustic potash is boiled:

$$2KOH + 2KMnO_4 = 2K_2MnO_4 + O + H_2O.$$

The same change occurs when reducing agents such as alcohol and sodium thiosulphate are added to the alkaline solution, only so much of course being added as suffices for the reduction of the permanganate to manganate. The red alkaline solution turns blue and afterwards green on exposure to air, this being caused by the reducing action of the organic matter contained in the atmosphere. This reaction explains the changes of colour in the mineral chameleon.

Potassium Manganate, K_2MnO_4, is formed when manganese dioxide is fused together with caustic potash. If the fusion takes place in the absence of air, the following reaction occurs:

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O.$$

Chevillot and Edwards found, indeed, that when the fusion

[1] *Ann. Phil.* xvi. 130, xvii. 150. [2] *Pogg Ann.* xxv. 287.

takes place in an atmosphere of nitrogen no manganate is formed. According to Elliot and Storer[1] this depends upon the fact that the manganate is decomposed in a current of nitrogen below a red-heat, whereas at a lower temperature, as at 180°, the manganate remains undecomposed. In the presence of air, or on the addition of nitre or chlorate of potash, a large quantity of the product is obtained. The deep-green coloured mass dissolves in a small quantity of water, forming a dark-green solution, from which, on evaporation in a vacuum, the salt separates out in small crystals isomorphous with those of potassium sulphate. If a concentrated solution of potassium permanganate be boiled with concentrated potash solution as long as oxygen is evolved a crystalline powder of manganate separates out on cooling, and if this be dissolved in dilute caustic potash and allowed to evaporate under the receiver of an air-pump, well-formed crystals of manganate are obtained. These are almost black, and possess a metallic lustre, but become green on exposure to the air.[2]

Sodium Manganate, Na_2MnO_4, is formed when a mixture of equal parts of manganese dioxide and soda-saltpetre is heated for sixteen hours; the mass is then lixiviated with a small quantity of water and the solution cooled down, when the salt separates out in small crystals isomorphous with Glauber-salt, and having the composition $Na_2MnO_4 + 10H_2O$. These dissolve in water with partial decomposition, yielding a green solution.

Barium Manganate, $BaMnO_4$, is formed when manganese dioxide is heated with baryta or barium carbonate or nitrate, or when barium permanganate is heated with baryta water. It is an emerald-green powder, consisting of microscopic four-sided prisms or six-sided plates. It has a specific gravity of 4·85, and is insoluble in water, but readily decomposed by acids. The employment of this salt in place of the poisonous Scheele's green has been suggested,[3] and it has been employed in a few instances, though not so generally as might be wished.

326 *Manganese Heptoxide*, Mn_2O_7, and *Permanganic Acid*, $HMnO_4$. The first of these compounds, also termed permanganic anhydride, was noticed by Chevillot, and more recently investigated by Thenard,[4] Aschoff,[5] and Terreil.[6] In order to

[1] *Proc. Am. Acad. Art. Sci.* v. 192.
[2] Aschoff, *Pogg. Ann.* cxi. 217.
[3] Schad, *Deutsch Industriezeit*, 1865, 118; Rosentiehl, *Dingl. Polyt. Journ.* clxxvii. 409.
[4] *Compt. Rend.* xlii. 389.
[5] *Pogg. Ann.* cxi. 217.
[6] *Bull. Soc. Chim.* 1862, 40.

prepare this compound, pure potassium permanganate free from chlorine is gradually added to well-cooled highly concentrated sulphuric acid. The salt dissolves with an olive-green colour, and at the same time oily drops separate, which gradually sink, forming a dark reddish-brown liquid which does not solidify at $-20°$. This liquid is extremely unstable, constantly evolving bubbles of oxygen on exposure to the air. These carry with them a small quantity of the heptoxide, and thus violet fumes are emitted. It rapidly absorbs moisture, and dissolves in water, yielding a deep violet-coloured solution, so much heat being thereby evolved that the liquid undergoes partial decomposition. It dissolves in concentrated sulphuric acid with an olive-green colour. On heating, it decomposes with evolution of light and heat, and with violent explosion. The same thing takes place when the heptoxide is brought into contact with any organic body, such as paper, or when a drop is allowed to fall into a vessel containing the vapour of alcohol, or into ether, or sulphuretted hydrogen.

327 *Permanganic Acid*, $HMnO_4$, is obtained in aqueous solution by adding the requisite quantity of dilute sulphuric acid to the barium salt. A deep red liquid is thus obtained, which exhibits a blue colour by reflected light, and possesses a bitter metallic taste. It decomposes on exposure to light, or when heated gently, and still more rapidly when boiled, with evolution of oxygen and separation of the hydrated dioxide. It acts as a most powerful oxidising agent, and decomposes ammonia:

$$6\,HMnO_4 + 8\,NH_3 = 3\,Mn_2O_2(OH)_2 + 4\,N_2 + 12\,H_2O.$$

Permanganic acid also occurs when manganese nitrate or any manganous salt, with the exception of the haloid compounds, is warmed with nitric acid and lead dioxide.

Potassium Permanganate, $KMnO_4$, is prepared on the large scale by a process which will be described further on. For laboratory purposes it is best obtained according to the process given by Gregory. This consists in dissolving ten parts of caustic potash in the smallest quantity of water, then adding to this a mixture of seven parts of potassium chlorate and eight parts of manganese dioxide, evaporating the whole to dryness, and heating the residue until the potassium chlorate is completely decomposed. The dark-green mass is then lixiviated with boiling water, the solution allowed to deposit, and the liquid filtered through asbestos or gun-cotton. The clear solution deposits the crystals on standing.

Potassium permanganate is isomorphous with potassium perchlorate, with which it crystallises in all proportions. The crystals are almost black, and when freshly prepared possess a green metallic lustre, which however on exposure to the air becomes of a steel-blue tint without any further alteration in the salt taking place. The crystals have a specific gravity of 2·7, and yield a red powder. They dissolve in fifteen to sixteen parts of cold water (Mitscherlich), forming a deep purple-coloured solution. When concentrated sulphuric acid is poured on to these crystals they decompose with evolution of light and heat evolving ozone and giving rise to violet-coloured vapours (Wöhler). On heating to 240° they decompose as follows:

$$2\,KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

Jones [1] has shown that hydrogen, phosphine, and other reducing agents decompose potassium permanganate, and that oxygen gas is evolved together with carbon dioxide when sulphuric acid acts on the permanganate in presence of oxalic acid.

Mixed with sulphur or phosphorus, a material is obtained which takes fire or explodes violently on percussion, and a mixture of the salt with charcoal burns like tinder.

Sodium Permanganate, $NaMnO_4$, is obtained in a similar way to the potassium salt, and is distinguished from it by being deliquescent, and, therefore, crystallising with difficulty.

Ammonium Permanganate, NH_4MnO_4 is obtained by the decomposition of the potassium salt with ammonium sulphate. It is isomorphous with potassium permanganate, and decomposes readily on heating.

Barium Permanganate, $Ba(MnO_4)_2$, forms hard, almost black prisms, soluble in water. It is obtained by passing a current of carbon dioxide through water containing barium manganate in suspension, or by the action of barium chloride on silver permanganate.

Silver Permanganate, $AgMnO_4$, separates out in large regular crystals when warm solutions of nitrate of silver and potassium permanganate are mixed. It dissolves in 190 parts of water at 15°, and is much more soluble in warm water. The solution decomposes on boiling.

Permanganic Oxychloride, MnO_3Cl. This chloride of permanganic acid was first prepared by Dumas: [2] he did not however analyse the compound, but from its mode of decomposition con-

[1] *Chem. Soc. Journ.* 1878, 95. [2] *Ann. Chim. Phys.* [2], xxxvi. 81.

sidered it to be manganese heptachloride, $MnCl_7$. It is obtained by gradually adding fused sodium chloride to a solution of potassium permanganate in concentrated sulphuric acid. A yellow gas is then evolved, which when passed through a freezing mixture condenses to a greenish-brown liquid. This when exposed to the air emits a purple-red vapour, which possesses the peculiar smell of the oxides of chlorine, and like them acts most violently upon the mucous membranes, so that the smallest quantity of the chloride contained in the commercial permanganate can thus be readily detected.[1] When heated it explodes violently, and water decomposes it with formation of permanganic acid and hydrochloric acid. These substances however mutually decompose with formation of free chlorine and manganese dioxide.

328 *Condy's Disinfecting Liquid.* Potassium permanganate has been employed for a long time in the laboratory as a powerful oxidising agent and is largely used in volumetric analysis. Hofmann was the first, in the year 1859, to show that this salt together with the other manganates and permanganates act as valuable disinfecting agents, and its application for this purpose has become now so general that these compounds, which a few years ago were only found in the laboratory, are now manufactured by the ton. The credit of this general application is mainly due to Mr. H. B. Condy, of London. For disinfecting purposes it is not necessary to employ the pure, well-crystallised salt, which is used in the laboratory, but a commercial article consisting of a mixture, more or less pure, of manganate and permanganate of sodium is used. This substance is obtained by mixing the caustic soda obtained from 1,500 kilos of soda-ash with 350 kilos of finely-divided manganese dioxide in a flat vessel, and heating this mixture for forty-eight hours to dull redness. The product is then lixiviated with water, and the solution either boiled down to the requisite degree of strength or e aporated to dryness. If the manganate is to be completely converted into permanganate it is neutralised with sulphuric acid, the solution concentrated until Glauber-salt separates out, and these crystals are then removed and the liquid further evaporated.[2]

[1] Aschoff, *Pogg. Ann.* cxi. 217.
[2] Hofmann's *Report Exhib.* 1862, p. 109.

MANGANESE AND SULPHUR.

329 *Manganese Monosulphide*, MnS, occurs as the mineral manganese-blende, or alabandite, forming a steel-grey crystalline mass, and sometimes observed in cubes and octohedrons. It has a specific gravity of 4·04, and occurs in veins in the coal-mines in Transylvania, and in Freiberg and Mexico. It may be obtained artificially in the form of a dark-grey powder, which melts at a high temperature forming a steel-grey crystalline mass, by heating the monoxide, the carbonate, or the sulphate in a current of hydrogen sulphide (Arfvedson). Ammonium sulphide and the other monosulphides of the alkali-metals precipitate hydrated manganese sulphide from a solution of a manganous salt in the form of a light flesh-coloured precipitate, which dissolves readily in dilute acids and oxidises on exposure to the air, assuming a brown tint. When left in contact or heated with an excess of ammonium sulphide it is transformed into a grey powder,[1] having the composition $3MnS + H_2O$.

Manganese sulphide combines with the sulphides of the alkali metals to form salts.[2] The potassium salt, $K_2S + 3MnS$, is formed when the anhydrous sulphate of manganese is gradually heated to redness, with three parts of potassium carbonate and 0·2 parts of lamp-black and excess of sulphur. The fused mass is treated with cold water freed from air, when a dark-red crystalline mass remains behind, which appears to be in micaceous transparent scales. In the dry state this compound is stable, but in the moist state it readily undergoes oxidation, becoming black and opaque, and when heated with nitre a violent explosion occurs.

Manganese Disulphide, MnS_2. This substance is found as the mineral hauerite in crystals belonging to the regular system. They possess a metallic adamantine lustre, and a reddish-brown colour, and occur at Kalinka in Hungary in clay together with sulphur and gypsum.

Detection and Estimation of Manganese.

330 Manganese is distinguished by forming a flesh-coloured sulphide readily soluble in dilute acids. In the course of analysis manganese is thrown down with the sulphides of the metals

[1] Muck. *Zeitsch. Anal. Chem.* v 580, vi. 6.
[2] Völker, *Ann. Chem. Pharm.* lix. 35.

of the present group and with others which are precipitated by sulphide of ammonium. If the precipitate be treated with very dilute cold nitric acid, the sulphides of cobalt and nickel, if present, remain undissolved. The solution is heated with potassium chlorate in order to remove the sulphuretted hydrogen, and an excess of caustic soda is added. Iron, manganese, and uranium are thus thrown down as hydroxides. The washed precipitate is then dissolved in hydrochloric acid, and the liquid neutralised with ammonia, and sal-ammoniac added, when the whole of the metals, with the exception of manganese, are thrown down and the filtrate is then evaporated to dryness, and the residue heated to get rid of ammoniacal salts. The mass which remains can be treated in various ways for the detection of manganese. The simplest plan is to fuse a small quantity of the residue with caustic soda and saltpetre, when the dark-green potassium manganate is formed, and this colour becomes deep blue on cooling. It dissolves in water with a green colour, which on addition of a little nitric acid turns red. Other characteristic reactions for the manganese salts are the following. Potash and soda precipitate the white hydroxide, which soon becomes brown on exposure to air. Ammonia in the presence of sal-ammoniac produces no precipitate. The solution rapidly absorbs oxygen from the air, brown manganic hydroxide being deposited. When a manganese compound is fused in a borax bead an amethyst-coloured bead is obtained in the outer flame, and this in the inner flame becomes colourless. The non-luminous gas-flame is coloured green by manganese chloride, and this exhibits a spectrum in which the metal-lines in the green and yellow are the following:[1]

$$\alpha = 5587 \qquad \beta = 5392 \qquad \gamma = 5195.$$

The spark-spectrum of manganese contains a large number of bright lines, of which the following are the most important (Lecoq de Boisbaudran):

Orange	Green	Blue	Indigo
6020·7	4822·8	4764·7	4230·8
6015·6	4782·6	4761·5	4224·7
6012·5		4753·4	

The absorption-spectrum of permanganic acid and its potassium salt exhibits in very dilute solution five distinct bands; a more concentrated solution gives continuous absorption in the yellow

[1] Hoppe-Seyler, *Journ. Pr. Chem.* cx. 303.

and green; and this is also observed in certain solutions of manganic salts. The latter, however, do not give the bands on dilution.

331 In order to determine manganese quantitatively it is usually precipitated as the carbonate. Frequently, however, it is thrown down as the hydroxide or peroxide. These are then converted by ignition into the red oxide, Mn_3O_4, in which condition the manganese is weighed. The sulphide on heating in the air is also converted into the same oxide.

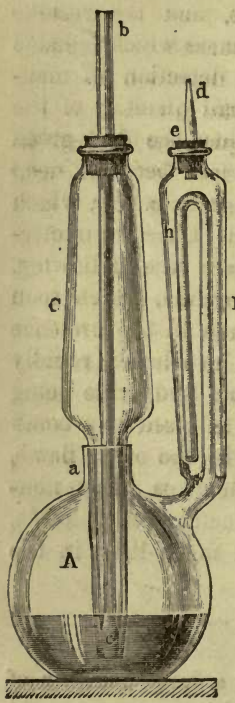

Fig. 132.

Manganese always occurs in nature together with iron. In order to determine this quantitatively, the solution is heated with sal-ammoniac, neutralised with the requisite quantity of ammonia, and the iron precipitated with succinate of ammonia. The manganese can then be determined in the filtrate in the above way.

Evaluation of Manganese Ores. The most accurate and convenient methods for the assay of manganese ores are those of Bunsen,[1] and of Fresenius and Will.[2] By the former method the quantity of chlorine which is evolved on treatment with hydrochloric acid is directly determined:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The free chlorine is collected in a solution of potassium iodide, and the liberated iodine estimated with a dilute solution of sulphurous acid.

Fresenius and Will's gravimetric method depends upon the fact that when manganese dioxide and oxalic acid are brought together in presence of sulphuric acid, the following decomposition occurs:

$$MnO_2 + C_2O(OH)_2 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

Or 87·78 parts of carbon dioxide correspond to 86·72 parts of manganese dioxide. From two to four grains of the finely-

[1] *Chem. Soc. Journ.* viii. 219. [2] Liebig's *Ann.* xlvii. 87.

powdered ore are brought into the vessel (A), Fig. 132, and from five to six grains of neutral oxalate of potash, together with some water, added. B and C are filled with concentrated sulphuric acid, and after the whole apparatus has been weighed, the acid is allowed to run from B into A, the operation being conducted as described under carbonic acid in Vol. I. p. 639. According to the experiments of Jones, oxygen is evolved in the above reaction together with carbon dioxide, in quantities, however, insufficient to interfere with the accuracy of the method.

The *atomic weight* of manganese has been determined by a variety of chemists. Berzelius[1] found that 4·20775 parts of manganous chloride yielded 9·575 parts of silver chloride, whence the atomic weight 54·86 is calculated. Five similar determinations by Dumas[2] gave the number 54·83; and V. Hauer[3] by reducing manganous sulphate to sulphide in a current of hydrogen sulphide, obtained the number 54·98.

IRON (FERRUM). Fe = 55·9.

332 Iron is the most important of all the metals. It seldom occurs in the metallic state in nature; the ores of iron are, however, found widely distributed, and usually in a state of purity; and the reduction of metallic iron may well be considered as one of the simplest of metallurgical operations, requiring far less knowledge and skill than is needed for the preparation of bronze. In spite of these facts it is usually supposed that the iron age followed that of bronze, although in many cases the art of working in iron became known at a very early period. It is however to be remembered that metallic iron is rapidly destroyed by rusting, at any rate in damp situations, and this may to some extent account for the comparatively rare occurrence of very early iron implements.

It appears probable that iron was first obtained from its ores in India, and it is certain that both the Assyrians and the Egyptians employed iron implements many centuries before our era. In the Pentateuch the metal iron is mentioned, as well as the furnaces in which it was prepared; the Hebrew name for

[1] *Pogg. Ann.* xiv. 211 [2] *Ann. Chem. Pharm.* cxiii.
[3] *Wien Acad. Ber.* xxv. 124.

iron, Barzél, is derived from the root Bazal, which signifies to be hard, whilst the derivation of the Greek word σίδηγος which occurs in Homer is unknown. The Greeks obtained their iron from the Chalybes, a nation dwelling on the south coast of the Black Sea, from whom the Asiatic nations also obtained iron. The Romans on the other hand not only procured their iron from this district, but also from Spain, Elba, and Noricum. The Elban iron mines, which are to this day renowned for their fine specular iron, were worked by the Etruscans, and the method which was employed by them for the extraction of the iron is identical in principle with that still in vogue in the Pyrenees.

The word iron, which is identical with the Scandinavian "iarn" (instead of "isarn"), and with the German "Eisen" (adjective, "eisern"), appears to be connected with the Sanscrit "ayas" (Latin "aes"), and this, according to Grimm, is an indication that bronze was in use among the Germans at a much earlier date than iron. The alchemists connected iron with the god of war Mars, and gave to it the sign ♂.

333 Native iron occurs, according to Andrews,[1] in small spiculæ distributed throughout the basalt of the Giant's Causeway, as well as in the old lavas of the Auvergne. The occurrence of terrestrial iron in large lumps has also not unfrequently been observed: these masses have however been formed in the firing of coal-pits when the burning mass has come in contact with ores of iron, and the product of the action is termed natural steel.

Fig. 133.

The native metal occurs more frequently in the form of *meteoric iron*. The meteorites falling in larger or smaller masses from extra terrestrial sources may be divided into two groups, "Earthy meteorites," which chiefly consist of silicates, and "Meteoric irons," which consist of meteoric iron together with a larger or smaller quantity of nickel, the presence of this latter metal being characteristic of meteoric masses. Meteoric iron likewise usually contains small quantities of cobalt and other metals, as well as graphite, ferrous sulphide and schreibersite, Ni_2Fe_4P, this last compound being one which does not exist in any terrestrial mineral. When the surface of a meteoric iron is planed and polished, and then treated with dilute nitric acid, peculiar configurations make their appearance which were first

[1] Andrews, *Brit. Assoc. Reports*, 1852.

noticed by Widmanstätten in the year 1808. These consist of rhombic folia or crystalline markings (shown in Fig. 133) which have a metallic lustre; the spaces enclosed by these markings are somewhat raised, so that a surface of meteoric iron thus treated may be used as a plate from which an engraving can be obtained. Some meteoric irons do not exhibit these figures, parallel striæ making their appearance when the metal is subjected to a similar treatment. Meteoric iron frequently occurs in considerable masses; thus, for instance, that which was discovered by Pallas in Siberia originally weighed 800 kilos [Analysis (*a*)], whilst that found in Bahia weighed nearly 7,000 kilos; a still larger mass occurs at Chaco-Gualamba in Peru, which is said to weigh 16,000 kilos, and similar large masses have been found in other localities both in North and South America, as well as in Africa. The largest known masses are those found at Ovifak on the island of Disko, off Greenland, where fifteen blocks of meteoric iron occur, the weight of the two largest being, according to Nordenskjöld [1] 21,000 and 8,000 kilos [see Analysis (*b*)].

The following table gives the composition of several meteoric irons:—

	(*a*)	(*b*)	(*c*)	(*d*)
Locality . . .	Siberia.	Ovifak.	Brazil.	Tennessee.
Analyst . . .	Berzelius.	Nordenskjöld.	Damover.	J. L. Smith.
Iron . . .	88·04	84·49	63·69	91·15
Nickel . .	10·73	2·48	33·97	8·01
Cobalt . .	0·46	0·07	1·48	0·72
Copper . .	0·07	0·27	0·05	0·06
Manganese	0·13	—	—	—
Carbon . .	0·04	10·62	0·02	—
Sulphur .	trace	1·52	0·02	—
Phosphorus	—	0·20	0·05	—
Chlorine .	—	0·72	—	—
Silicate . .	0·53	0·09	—	—
	100·00	100·46	99·28	99·94

Finely divided meteoric iron is constantly falling from extra-terrestrial space on to the earth: the occurrence of this meteoric dust has been observed in Sweden and in the snow-fields of Northern Siberia, the snow enclosing black magnetic particles which contain cobalt as well as iron. More recently similar particles of meteoric dust, consisting of metallic iron, have been

[1] *Pogg. Ann.* 151, 154.

found by Mr. Murray, of the *Challenger* expedition, at great depths in mid-ocean. It is only under conditions such as the above that it is possible to detect this fine meteoric dust in consequence of the enormous accumulation elsewhere of terrestrial dust.

334 Iron is usually found in combination either with oxygen or sulphur. Of the large number of minerals which contain iron only those will now be mentioned which occur most commonly and in largest quantity; the ores will be specially described hereafter. The most important oxygen compounds of iron are red hæmatite, or specular iron, Fe_2O_3; brown hæmatite, $Fe_4O_3(OH)_6$; magnetic iron, Fe_3O_4; spathose iron, $FeCO_3$, which latter also contains other isomorphous carbonates. Again, iron pyrites, FeS_2, occurs largely, whilst magnetic pyrites, Fe_7S_8, is less common; ferrous sulphide also forms an important constituent of copper pyrites, $CuFeS_2$, arsenical pyrites, $Fe(AsS)_2$, and other minerals. Silicates of iron are found in most geological formations, and from these iron oxide finds its way into the soil, in which it is usually present in considerable quantity, imparting to it a reddish or brown colour. This fact was known to Pliny, who mentions that the presence of iron may be recognised by the colour of the soil. Iron compounds are contained in solution in spring- and river-waters, as well as in the water of the ocean, and it is from one or other of these sources that plants obtain the iron which forms a necessary constituent of their chlorophyll.

In 1702 N. Lemery proved that the ashes of plants contain iron: this observation was confirmed by the experiments of Geoffroy in 1705, who, however, assumed that the iron is not originally contained in plants, but that it is produced when they are burned. Other celebrated chemists, such as Becher, held the view that the iron which makes its appearance when certain substances are subjected to chemical treatment is not contained in them but is independently produced. This erroneous opinion was first disproved by Lemery.

Iron likewise forms a necessary constituent of the animal body; thus for instance, hæmoglobin, the red colouring-matter of the blood, contains 0·24 per cent. of iron. Iron preparations have also long been employed as a medicine, especially in chlorosis, general debility, and loss of blood; and it has now been ascertained that after the use of iron the number of red corpuscles is increased, and the amount of hæmoglobin which

they contain becomes larger. At the same time the nutritive processes of the body are accelerated, as evidenced by a rise in temperature, and an increase in the quantity of urea secreted. The presence of iron in the blood was first shown by Menghini of Bologna in 1747.

The existence of iron in large quantities in meteoric masses indicates a wide cosmical distribution of this element, and this conclusion has been confirmed by Spectrum Analysis, which indicates to us the presence of iron in the sun and many fixed stars.

335 *Preparation of pure Iron.*—Iron is usually produced from its oxides by means of charcoal, and is thus obtained on the large scale; thus prepared, however, iron is not pure, but contains more or less carbon. The purest commercial form of iron is wrought-iron, especially the finest kinds of harpsichord wire: this contains about 0·3 per cent. of foreign impurities chiefly consisting of carbon. In order to obtain chemically pure iron the oxide, or oxalate, may be heated in a current of hydrogen at the lowest possible temperature; the metal is obtained by this process as a black powder, which oxidises and becomes incandescent in the air, but if the reduction be carried on at a higher temperature the powdered iron is not pyrophoric.

Pure iron may be obtained by the reduction of ferrous chloride, $FeCl_2$, in hydrogen when the metal is deposited in microscopic quadratic octohedrons, or cubes (Peligot).[1] It may also be prepared by electrolyis. For this purpose a solution of ferrous sulphate is prepared and then mixed with sal-ammoniac and magnesium sulphate; on electrolysis the iron is deposited in bright grey plates. Electrolytic iron has the power of occluding certain gases, especially hydrogen; on heating the metal in a vacuum these gases are given off, and the metal which remains has a white colour resembling platinum. In order to obtain pure iron as a coherent metallic mass a mixture of equal parts of pure Glauber salt and iron sulphate is ignited in a platinum crucible until no further evolution of sulphur dioxide occurs; on washing the mass with water a crystalline precipitate of ferric oxide remains behind: this is next placed in a platinum crucible and reduced in hydrogen. The porous mass of reduced iron is then pressed into a lime crucible and melted by means of the oxy-hydrogen blowpipe.[2]

[1] *Compt. Rend.* 19, 670.
[2] Matthiessen and S. P. Szczepanowski, *Chem. News*, xx. 101.

Good wrought-iron when melted in this way also yields a regulus of pure metal, especially if towards the end of the operation the current of oxygen be increased, when the impurities are oxidised and absorbed by the porous mass of the crucible.[1]

336 *Properties.* Pure iron has a specific gravity of 7·84; it possesses an almost silver-white lustre, and takes a high polish; it is the most tenacious of all the ductile metals except cobalt and nickel; it becomes soft at a red-heat, whilst at a white-heat it can be readily welded, but if heated above the welding-point it is brittle under the hammer. Pure iron is more difficultly fusible than wrought-iron, but it can be volatilised when heated in a vacuum by means of a powerful electric discharge, and if air be then admitted the vapourised iron burns with a bright flash. Even when iron is burned in oxygen a small quantity of the metal is vapourised and is seen to burn. Iron is attracted by the magnet and may also be rendered magnetic, but it loses this latter property after a short time, whilst carbonised iron or steel retains this polar condition at the ordinary temperature, losing it however at a red-heat. Iron does not undergo any alteration in dry oxygen or in pure air at the ordinary temperature, nor does it decompose water free from air even when warmed. In moist air, on the other hand, it becomes coated with ferric hydroxide, or iron rust, this oxidation being greatly assisted by the presence of carbon dioxide or small quantities of acid vapours. In contact with air and water, and with certain acids and salts, especially ammoniacal salts, this oxidation or rusting is promoted, whilst the liability to rust is diminished in the presence of alkalis. The formation of rust takes place to begin with but slowly, but if a very thin superficial coating of oxide has been formed the process goes on quickly. In order to diminish the liability to rust, iron articles are painted with varnishes, or oil-colours, or the surfaces are covered with oil, fat, or graphite. A coating of black magnetic oxide of iron, Fe_3O_4, serves, however, as the best protection against the rusting of iron. For the purpose of coating objects of iron with this oxide, Becquerel places the iron as the positive electrode in a solution of sulphate of iron and sal-ammoniac, whilst the process recently patented by Barff consists in exposing the iron to the action of superheated steam at a temperature of about 650°, when a film of hard magnetic oxide is formed on the surface,

[1] Troost, *Bull. Soc. Chem.* [2], 9, 250.

and this does not undergo any further change, and is said effectually to protect the metal.

In contact with metallic zinc iron becomes electro-negative, and is thus to a certain extent protected from rusting. Iron dissolves in most dilute acids with evolution of hydrogen. Dilute nitric acid dissolves it in the cold without the evolution of any gas and with the formation of ferrous nitrate, $Fe(NO_3)_2$, and ammonium nitrate; when heated, or when a stronger acid is employed, oxides of nitrogen are evolved and ferric nitrate, $Fe(NO_3)_6$, is formed.

Passive Iron. Under certain circumstances iron is not acted upon at all by nitric acid, nor does it, when in this condition, precipitate copper when brought into solutions of this metal. Iron in this state is termed passive, and this condition is brought about by dipping the metal into concentrated nitric acid and then washing it (Keir).[1] Other substances, such as chloric, bromic, iodic, and chromic acids, and even hydrogen dioxide, act upon iron in a similar way. According to Faraday and Beetz this passive condition of iron depends upon the formation of a very thin film of oxide, and this conclusion is confirmed by the fact that iron wire may also be made passive by a moderate ignition.

Iron combines readily with the elements of the chlorine group, and at a red-heat it burns in oxygen and the vapour of sulphur; it also combines with carbon when brought in contact with it at a high temperature, and for this reason all the iron obtained on the large scale contains carbon in combination; and the larger the quantity of this element it takes up the more readily fusible is the iron. Cast-iron contains the largest quantity, and wrought-iron the smallest quantity, of carbon, whilst steel contains an amount intermediate between these two.

337 *Iron amalgam* does not form readily, but on acting with a one per cent. sodium amalgam upon a solution of ferrous sulphate, a semi-solid mass is obtained which, when in small globules, is attracted by the magnet. On distilling this amalgam, metallic iron remains in a fine state of division (Böttger). The same amalgam can be formed by rubbing powdered iron with mercuric chloride and water. If an iron wire be attached to the copper-pole of a Daniell's element, the wire dipped into a solution of ferrous sulphate, whilst another iron wire from the zinc-pole touch a drop of mercury lying in the solution, amalgams of varying composition are obtained according to the

[1] *Phil. Trans.* 1790, 379.

intensity of the current. Those containing only small quantities of iron are liquid; those in which more iron is present are soft and crystalline. One containing 103·2 of iron to 100 of mercury forms a hard black mass obtained by pressing the liquid amalgam under a pressure of 50 tons on the square inch.[1]

METALLURGY OF IRON.

338 Several mythical stories point to the fact that in very early times meteoric iron, which falling from the heavens was considered as a gift of the gods to man, was employed in the manufacture of iron weapons. This indeed appears to be a practice still employed by certain uncultured tribes; the Esquimaux, as we hear from Ross, employ meteoric iron for the manufacture of their implements, and Kumbary [2] relates that the chiefs in the Wadai country, in Central Africa, possess many weapons which have been worked up from meteoric masses. But meteoric iron occurs so sparingly upon the earth's surface, and is in fact so unsuited to the manufacture of tough forgings, that at a comparatively early period in the history of civilisation men set about the smelting of iron from its ores.

The enormous deposits of ancient slag and furnace-cinder which are found spread over large areas in various districts of India point to the fact that the iron industry existed in that country at very early times, and even to the present day the manufacture of iron is carried on in India in the most primitive manner. It is also clear that the ancient Egyptians were well acquainted with the uses of iron, and the remains of their iron-works have recently been found near Sinai. But, independently of these sources, a knowledge of the methods of working iron ores also appears to have been gained by the tribes living in the North of Europe whilst the inhabitants of the Western Hemisphere were not acquainted with these processes. Little is known respecting the method employed by the ancients in the manufacture of iron; the slight information which we possess has been collected together by Agricola in his work, "De Veteribus et Novis Metallis." The apparatus employed was evidently of a primitive kind, and consisted of a small hearth or furnace to which was attached a bellows or blowing arrangement driven by hand, similar indeed to that which is now in

[1] Joule, *Journ. Chem. Soc.* [2], i. 378. [2] *Compt. Rend.* lxx. 649.

use among the hill-tribes in India and in Central Africa. Malleable iron and steel were both produced by igniting the iron ore with charcoal, the metal being obtained in the form of a porous lump or "bloom," which was pressed or hammered into a coherent metallic mass.

The dexterity exhibited by the Hindoos in the manufacture of wrought-iron may be estimated from the fact of the existence in the Mosque of the Kutub near Delhi of a wrought-iron pillar no less that 60 feet in length.[1] This pillar stands about 30 feet out of the ground, and has an ornamental cap bearing an inscription in Sanskrit belonging to the fourth century. It is not an easy operation at the present day to forge such a mass with our largest rolls and steam-hammers; how this could be effected by the rude hand-labour of the Hindoos we are at a loss to understand.

ORES OF IRON.

339 Before describing the several methods for preparing iron the various ores which serve for this preparation must be mentioned. The term iron-ore includes all those minerals which contain iron not only in a sufficient quantity, but also in a condition which enables them to be employed for the economic production of metal. Thus, for example, iron pyrites, FeS_2, although it occurs in very large quantities and contains a high percentage of iron, cannot properly be described as an iron-ore, inasmuch as it is difficult to completely remove the sulphur, a small proportion of which renders the metal unfit for use. In like manner arsenical pyrites, although it also contains a large quantity of iron, is unfit for the production of the metal; and the same may be said of many other minerals which contain large quantities of iron.

The various ores of iron are composed of, or contain, the oxides of iron in more or less pure condition, and the value of an iron ore depends rather upon the nature of the impurities which it contains than upon its percentage of iron.

The ores of iron occur almost in every geological formation; thus magnetic iron ore is found in the older rocks, as in the Laurentian beds of North America, and the old slates and gneisses of Sweden, whilst red hæmatite occurs in beds or pockets in

[1] A cast of this pillar is to be seen in the Architectural Court of the South Kensington Museum, and a drawing of the same is found in St. John Day's *Prehistoric Use of Iron and Steel*, p. 144.

the carboniferous limestone of Cumberland and North Lancashire, and spathose or clay iron-stone in the coal measures. Again, the oolitic rocks furnish large deposits of brown hæmatite, and the Elba ore is probably a tertiary deposit. Still more recent formations of iron ore are seen in the Bog ore of Germany and the North of Ireland, whilst "lake ores" are being formed in Scandinavia at the present day.

340 *Magnetic Iron Ore, Magnetite, Loadstone,* Fe_3O_4. This ore, in the pure state, constitutes the richest and most valuable ore of iron. It occurs in the crystalline and massive state as well as in the form of sand, and is found in large deposits, especially in volcanic rocks, as well as in granite, gneiss, and mica-schist. This ore of iron is difficultly reducible, but it yields excellent iron and steel. The most important localities of magnetite are Arendal, Dannemora, and other places in Norway, Sweden, and Lapland; the island of Elba; the Ural Mountains; and in several localities in the United States. In England magnetic oxide of iron occurs in Rosedale in Yorkshire, at Dartmoor, at Brent in South Devon, and at Treskerby in Cornwall; but it cannot be said to be an important English ore. In Germany it is found in large quantities at Schmiedeberg, in Silesia, and a few other localities.

The composition of some important Magnetites is given on p. 37.

These analyses show that the relation between the amount of the two oxides varies considerably according as the monoxide has been more or less oxidised to the sesqui-oxide. The pure crystallised mineral occurring at Berggieshübel, in Saxony, contains, according to Karsten, Fe_2O_3 69·24, FeO 30·49 per cent., and this proportion agrees approximately with the formula Fe_3O_4.

Franklinite, $(FeMn)_2O_3(FeZn)O$, occurs in New Jersey, and is first worked for zinc, the residue being used as an iron ore.

341 *Red Hæmatite,* or *Specular Iron Ore,* Fe_2O_3. This substance occurs crystalline as specular iron ore, and also in a massive state having a columnar, granular, or botryoidal form as well as in the earthy condition. This ore, being free from impurities, yields a cast-iron which is especially well adapted for the manufacture of malleable iron and steel. Hæmatite occurs in veins as well as in beds and pockets. One of its most remarkable localities is the island of Elba, where it occurs finely crystallised between talcous schist and crystalline limestone. The Elban mines were worked by the Etruscans and are still

Analyses of Magnetic Iron Ores.

Source	Dannemora.	Elba.	Schmiedeberg.	Michigan Mine, Lake Superior.	New York State.	
					Port Henry, No. 1, Selected.	Split Rock.
Analyst	Ward and Noad.	Jordan.	Grundmann.	Ralph Crooker.	Prof. Chandler.	G. W. Maynard.
Magnetic oxide of iron	—	—	—	—	95·99	—
Sesquioxide of iron	62·06	62·00	54·82	61·631	—	38·43
Protoxide of iron	28·42	24·00	24·67	29·109	—	23·40
Protoxide of manganese	—	0·80	—	traces	0·10	0·23
Alumina	—	—	5·94	2·120	2·00	0·34
Calcium carbonate	—	—	4·40	—	—	—
Lime	—	—	—	1·070	0·52	3·54
Magnesia	1·44	—	—	—	0·60	2·13
Sulphur	—	—	—	0·002	0·10	—
Sulphuric acid	—	—	—	0·008	—	—
Phosphoric acid	—	—	—	0·057	0·10	—
Ferrous sulphide	0·07	0·20	6·99	—	—	—
Water	—	—	—	1·497	—	—
Carbonaceous matter	—	—	—	0·340	—	—
Titanic oxide	—	—	—	0·032	—	14·70
Silica	—	—	—	3·280	0·64	16·46
Silica and insoluble residue	7·60	13·00	3·18	—	—	—
	99·59	100·00	100·00	99·146	100·05	99·23

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productive. A fine hæmatite occurs in the Huronian rocks on the southern shore of Lake Superior, whilst at Iron Mountain, near St. Louis, Missouri, enormous masses of this ore of iron are found. On the continent of Europe hæmatite occurs in Belgium, and on the Lahn in Westphalia deposits of this ore are found in the Devonian formation. The chief deposits of hæmatite in England are those near Ulverston in Lancashire, and on the coast of Cumberland near Whitehaven; the ore here occurs in beds or pockets in the carboniferous limestone, sometimes existing as hard botryoidal masses exhibiting crystalline structure, and sometimes in a soft or compact amorphous condition.

The specular iron from Elba occurring in large crystals consists, according to Rammelsberg, of iron peroxide together with 0·3 per cent. of titanium dioxide, sometimes as much as 0·8 of iron monoxide and 0·4 per cent. of magnesia. American hæmatites are also frequently extremely pure; thus Jordan found an ore from Michigan contained the following impurities: 0·09 lime, 0·11 magnesia, 0·28 insoluble residue. The ore as employed for the production of iron is always more or less mixed with "gangue," as is shown from the Analyses on p. 39.

342 *Brown Hæmatite, or Limonite,* $Fe_2O_3+Fe(OH)_6=2Fe_2O_3+3H_2O$. This substance occurs crystallised in rhombic prisms, but is more frequently found either in a fibrous foliated and scaly condition, or as a dark brown reniform mass and commonly known as Brown and Yellow Hæmatite. In the massive state this ore occurs in large quantity and, as it can be readily worked, it has been long employed as a source of iron (for analyses see table on p. 40). It is found in the carboniferous limestone as well as in the older rocks, in the Forest of Dean, and at Llantrissant in Glamorganshire in the lower coal-measure sandstones. At Bilboa in Spain it occurs largely in carboniferous limestone, whilst the newer and earthy brown hæmatite is found in the oolite and green-sand in Northamptonshire and Lincolnshire. It is likewise largely worked in Germany and France, being the ore from which the greater part of the iron made in these countries is derived. The bog-ores which are worked in the plain of North Germany and Canada and in other places, as well as the peculiar iron ore of the North of Ireland and the Swedish lake-ore, belong to this class, and are of the most recent geological formation.

343 *Spathose Iron Ore, or Siderite.* Spathose iron ore consists

Analyses of Red Hæmatite Ores.

Source . . .	Cleator Moor, Cumberland.	Ulverston (Unctuous) Cumberland.	Willmansdorf.	Wetzlar.	Jackson Mine, Lake Superior.	Negunnee. Manganiferous Soft Hæmatite.	Fossiliferous from Tennessee (fish-egg ore).
Analyst . . .	Dick and Spiller.	Dick.	Ziureck.	Streng.	Chandler and Cairns.	Chandler and Cairns.	G. W. Maynard.
Ferric oxide	95·16	86·50	92·68	43·58	93·75	65·40	76·96
Manganous oxide . .	0·24	0·21	—	trace	trace	6·71	0·66
Alumina	—	—	2·80	1·42	0·73	1·46	7·60
Lime	0·07	2·77	—	—	0·61	0·45	0·62
Magnesia	—	1·46	—	—	0·23	0·66	0·48
Sulphur	—	—	—	—	0·03	0·04	0·12
Sulphur trioxide . .	trace	0·11	—	0·20	—	—	—
Carbon dioxide . . .	trace	2·96	—	—	—	—	—
Phosphorus pentoxide.	trace	trace	—	trace	0·32	0·16	0·85
Water and organic matter	—	—	—	—	1·09	2·46	3·14
Silica	—	—	—	—	3·27	22·67	9·38
Silica and insoluble residue	5·68	6·55	4·52	55·22	—	—	—
	101·15	100·56	100·00	100·42	100·03	100·01	99·81

Analyses of Brown Hæmatites.

Source	Forest of Dean.	Llantrissant.	Hamm.	Spain.	Oolite rocks, Northamptonshire.	Limonite. Tennessee.	Bog Ore. Neumark.	Lake Ore. Smaland.
Analyst	A. Dick.	E. Riley.	Schnabel.	A. Baker.	Spiller.	G. W. Maynard.	Karsten.	Svanberg.
Ferric oxide	90·05	59·05	75·70	78·80	52·86	83·69	49·60	65·58
Manganous oxide	0·08	0·09	—	0·65	0·51	—	1·10	3·87
Alumina	trace	trace	—	3·50	7·39	trace	—	5·09
Lime	0·06	0·25	—	trace	7·46	—	1·40	0·82
Magnesia	0·20	0·28	—	trace	0·68	—	—	0·15
Carbon dioxide	—	—	—	—	4·92	—	—	—
Phosphorus pentoxide	0·09	0·14	2·67	0·07	1·26	0·38	5·60	1·13
Sulphur trioxide	trace	—	—	—	—	—	—	trace
Sulphuric acid	—	—	—	—	—	0·34	—	—
Silica	—	—	—	—	13·16	2 60	—	—
Ferrous sulphide	—	0·09	—	—	0·03	—	—	—
Water	9·22	6·38	13·32	11 65	11·37	12·80	23·10	16·21
Organic matter	—	—	—	—	—	0·19	—	—
Insoluble residue	1·07	34·40	7·61	5·55	—	—	19·20	7·15
	100·77	100·68	99·30	100·22	99·54	100·00	100·00	100·00

of ferrous carbonate, $FeCO_3$, invariably mixed with the isomorphous carbonates of manganese, magnesium and calcium. It possesses a yellowish-brown colour, and occurs often in globular or botyroidal forms having a silky fibrous structure. It is usually found in Devonian rocks, occurring in England at Brendon Hill in Somerset, at Exmoor and at Weardale in Yorkshire. The most celebrated European locality is the Erzberg in Styria, where not less than 110,000 tons of ore are annually raised and used for the manufacture of the celebrated Styrian steel. Spathose iron ore also occurs in large quantity in Carinthia, at Stahlberg near Müsen, and at Siegen in Prussia.

Analyses of Spathose Iron Ore.

Source—	Weardale.	Erzberg.	Stahlberg, Müsen.
Analyst—	Tookey.	Karsten.	Schnabel.
Ferrous oxide . . .	49·77	55·64	47·16
Ferric oxide . . .	0·81	—	—
Manganous oxide . .	1·93	2·80	10·61
Lime	3·96	0·92	0·50
Magnesia	2·83	1·77	3·23
Carbon dioxide . . .	37·20	38·35	38·50
Phosphorus pentoxide.	trace	—	—
Sulphur	0·04	—	—
Water	0·30	—	—
Insoluble residue . .	3·12	—	—
Total . . .	99·96	99·48	100·00

344 *Clay Iron-stone or Argillaceous Iron Ore* is a spathose iron containing clay or sand, and is chiefly found in nodules or bands interspersed throughout the clays and shales of the coal-measures. This ore is the most important English ore of iron, as fully one-half of the iron made in this country is reduced from clay iron-stone. The chief workable beds of British clay iron-stone occur in Yorkshire, Derbyshire, Staffordshire, Warwickshire, South Wales and Scotland.

The "black band" iron-stone is an important variety of this

ore. It contains from 20 to 25 per cent. of coal, and is found in Lanarkshire, North Staffordshire, and South Wales. The Scotch beds were discovered by Mushet in 1800, but they were not worked until the year 1830. In 1855 the same ore was discovered in Westphalia, and it is also worked in Lower Silesia. The coal-measures of the Gard and of the Aveyron in France, and those in Pennsylvania and Maryland and other States, also contain large quantities of clay iron-stone. The same ore is found in strata in the Lias and also in the Oolitic and Tertiary rocks, the Cleveland iron ore belonging to this latter class. Analyses of several clay iron-stones are given on p. 43.

IRON SMELTING.

345 *Calcination of the Ore.*—Before treatment in the furnace many iron ores, especially the clay iron-stones and the brown hæmatites, are subjected to a process of calcination or roasting. The object of this is to expel water and carbonic acid, and also to oxidise the ore as well as to render it more porous, and thus to facilitate the subsequent reduction of the metal. At the same time any sulphides which the ore may contain are oxidised and the sulphur expelled. The ordinary clay iron-stone is usually roasted in large open heaps, the ore being mixed with a sufficient quantity of coal to keep up a slow combustion. A preferable method is to calcine the ore in kilns or roasters, as in these the consumption of fuel is less and the product more uniform than in the ruder process of roasting in heaps.

(I.) The Direct Reduction of Malleable Iron from the Ores.

346 *Iron Furnaces.*—The simplest form of the iron furnace is that used at the present day on the west coast of India, as well as in the Deccan and Carnatic, and amongst the hill tribes. The low-caste Hindoos who work in iron, wander from place to place and build up their simple apparatus where they find fuel and ore; this latter consisting generally of magnetic oxide or brown hæmatite. The furnaces are built on the ground and constructed in the form of a round shaft or chimney, from 2 to 4 feet in height, having a diameter at the bottom of from 10 to 15 inches, and at the top of from 6 to 12 inches. At the lower part there are two openings one of which serves for the

Analyses of Clay Iron-stone.

Source . . .	Lowmoor, Yorkshire.	Butterley, Derbyshire.	Pin's Ore. Dudley, Staffordshire.	Pontypool, South Wales.	Scotland. Black Band.	Cleveland. Iron Ore.
Analyst . . .	Spiller.	Spiller.	Dick.	Riley.	Colquhoun.	A. Dick.
Ferric oxide	1·45	1·49	0·54	0·59	2·72	3·60
Ferrous oxide	36·14	37·99	45·35	44·50	40·77	39·92
Manganous oxide . . .	1·38	1·51	0·56	0·73	—	0·95
Alumina	6·74	5·57	5·70	5·95	—	7·86
Lime	2·70	4·59	2·60	2·05	0·90	7·44
Magnesia	2·17	3·37	1·26	3·26	0·72	3·82
Silica	17·37	10·04	10·63	10·81	10·10	7·12
Carbon dioxide . . .	26·57	29·92	30·21	30·92	26·41	22·85
Phosphorus pentoxide . .	0·34	0·80	0·46	0·23	—	1·86
Iron disulphide . . .	0·10	0·06	0·20	0·11	—	0·11
Alkalis	0·65	0·55	0·36	0·13	—	0·27
Water	1·77	3·21	1·64	0·76	1·00	2·97
Organic matter	2·40	1·42	1·59	0·21	17·38	1·64
	99·78	100·52	101·10	100·25	100·00	100·41

blast and the other for the exit of the slag which is formed by the silicates contained in the ore, as well as for the extraction of the bloom of iron. The bellows are usually made from a goat's-skin or a buffalo hide, furnished with bamboo tubes. As soon as the furnace is warmed with charcoal, layers of the broken ore and charcoal are built in the shaft, and after from 4 to 6 hours a porous bloom of iron is obtained, varying in weight from 5 to 30 lbs., and this is then worked under the hammer. Throughout Central India and in the north-east provinces the manufacture of iron is somewhat further advanced, the furnaces being larger and of a similar character to those which have been or are still in use in various parts of the world, as in Africa, Borneo, and certain parts of Europe. Even to the present day the direct reduction of malleable iron from the ores is carried on in some European localities, especially in the Pyrenees and in certain districts of Spain where a peculiar forge, termed the *Catalan forge*, is employed. The hearth of this furnace is about 3 feet long, 2 feet wide, and about 3 feet deep; at one side is an opening through which a *tuyère* is placed. The blast is supplied by the air carried down by a jet of falling water in a blowing machine termed a *trompe*. According to the size of the hearth the quantity of ore employed varies from 3 to 10 cwt. and this requires about its own weight, or rather more, of charcoal, and yields about 33 per cent. of iron. The ores employed are partly hæmatite and partly brown iron ore or spathose iron; the latter ores are previously roasted in order to expel water or carbon dioxide. At the beginning of the operation a weak blast is employed in order that the metal may be reduced by the carbon monoxide. The temperature is afterwards increased and blooms of metallic iron are obtained, which need only to be brought under the hammer to yield marketable bar iron. By a similar process the Elba specular iron has been worked up to within recent times in Corsica. In the United States, especially in districts where charcoal is plentiful, similar *bloomery forges* are still worked with a hot blast of air. Some of these forges are capable of turning out a bloom of 300 pounds weight every three hours. The high bloomery furnace or "Stückofen" of the Germans is a blast furnace formerly in use in Carniola, and elsewhere, for the direct production of iron from the ore by reduction with charcoal. The process is, however, an expensive one owing to the large quantity of charcoal needed, and it has been recently superseded by other and cheaper methods.

(II.) The Manufacture of Cast-Iron.

347 The indirect process for obtaining malleable iron may be divided into two stages, viz., first, the production of cast-iron; second, the subsequent manufacture of malleable or wrought iron.

The Blast Furnace.—The application of the blast furnace to the manufacture of iron marks an era in the history of the iron industry, inasmuch as it was by its use that a continuous process of iron manufacture became possible. The discovery of a process by which fusible cast-iron can be prepared, appears to have been made, probably accidentally, in Germany, about the end of the fifteenth century, where the Stückofen had long been in use for manufacturing blooms. No description of the process is, however, to be found in the older writers upon metallurgy. Thus Agricola, writing in 1556, only mentions the older methods of iron making, although he appears to have been acquainted with cast-iron; at any rate the new method must have been at work in this country in 1543, for we find that in that year English cast-iron cannons were used. The great demand for cast-iron, which was of course all made with charcoal, soon leading to a destruction of our forests, it became necessary, in the first year of the reign of Elizabeth, to endeavour to replace charcoal by some other fuel. This was accomplished by the employment of coke instead of charcoal, a practice carried out in England as early as the first half of the seventeenth century. The problem of smelting iron with pit coal was first successfully solved by Abraham Darby at Colebrookdale, about the year 1735.[1]

The blast furnace consists of a shaft varying in height from 50 to 90 feet, and the largest diameter from 14 to 17 feet. The essential parts of the furnace are: first, *the hearth*, or circular chamber, built of stone and lined with firebrick, and, in the second place, a shaft or chimney formed of two truncated cones joined at their bases, the upper being termed the "body," and the lower one the "boshes." Fig. 134 shows the construction of such an ordinary furnace. The shaft (A B C D) is 50 feet high, the throat (A) is 10 feet in diameter, and the shaft widens to the point (B), termed the belly, where it is 16 feet in diameter, diminishing again to

[1] For further interesting information on this subject the reader is referred to Percy's admirable "Sketch of the History of Iron," *Iron and Steel*, p. 873.

4 feet in the hearth (C D). The outer portion of the stack (G) is built of strong masonry; inside this is a lining of fire-brick (E),

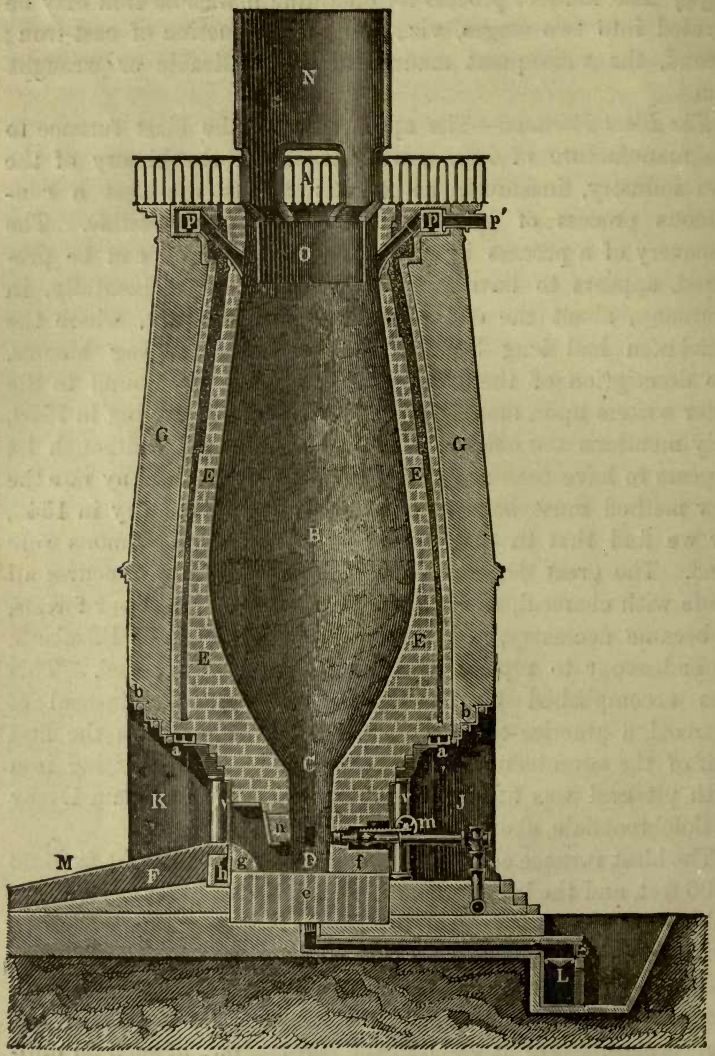


FIG. 134.

and between these is a cavity filled with tap-cinder or refractory sand; the object of this cavity is to allow the moisture to escape from the brickwork. To keep the whole well dry, the

foundations are traversed by arched galleries. The hearth is composed of slabs of refractory sandstone cemented with fire-clay, and the bottom of each is usually made of large fire-bricks supported on masonry. Only three sides of the hearth are built to the bottom; one ending within a short distance of the base, and being supported by a strong bearer of cast-iron, on which a block of refractory brick (*n*) rests; this is termed the *tymp*. A short distance beneath the tymp, and a little in front of it, is the *damstone* (*g*), fixed in position by a strong plate of iron, placed on its outer side, and termed the *damplate* (F). Over this damstone the slag flows on to the damplate in a continuous stream. The throat of the stack is generally surmounted by a chimney (N), below which the iron cylinder (O) is hung. The object of this cylinder is to collect the unburned combustible gases escaping from the throat, and to enable them to pass through the tubes (P P) for use in other parts of the works.

Fig. 135 shows the construction of the furnace by horizontal section at C.

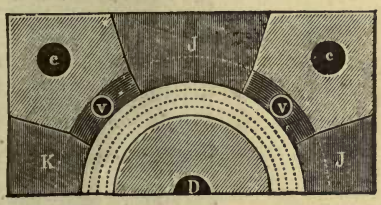


FIG. 135.

The construction of the modern blast furnaces is much less massive than that of the older ones, such as that which has just been described. They are termed cupola furnaces, and are entirely built of fire-bricks, either closely bound with hoops, or more frequently completely cased in boiler plate. Fig. 136 shows such a furnace lately erected at Dutton Brook, near Warrington. This is closed at the top with a contrivance called the "cup and cone" arrangement, first introduced by Mr. Parry at Ebbw Vale Works. It consists of an inverted cast-iron cup or funnel (*a*) fixed on the top of the throat of the furnace, and (*b*) a cast-iron cone suspended by a chain running over a wheel, and having a counterpoise at the other end. When the cone is raised against the cup the throat of the furnace is closed, and the escape of gases into the air prevented; these then pass out of the furnace by side openings, and are conveyed by pipes to any point where the heat caused by their combustion can be made available.

The blast is introduced at the bottom of the furnace through tuyère holes perforating the walls of the hearth. The tuyères are made of cast or wrought iron, and have a double casing,

through which water circulates to keep them cool; they vary

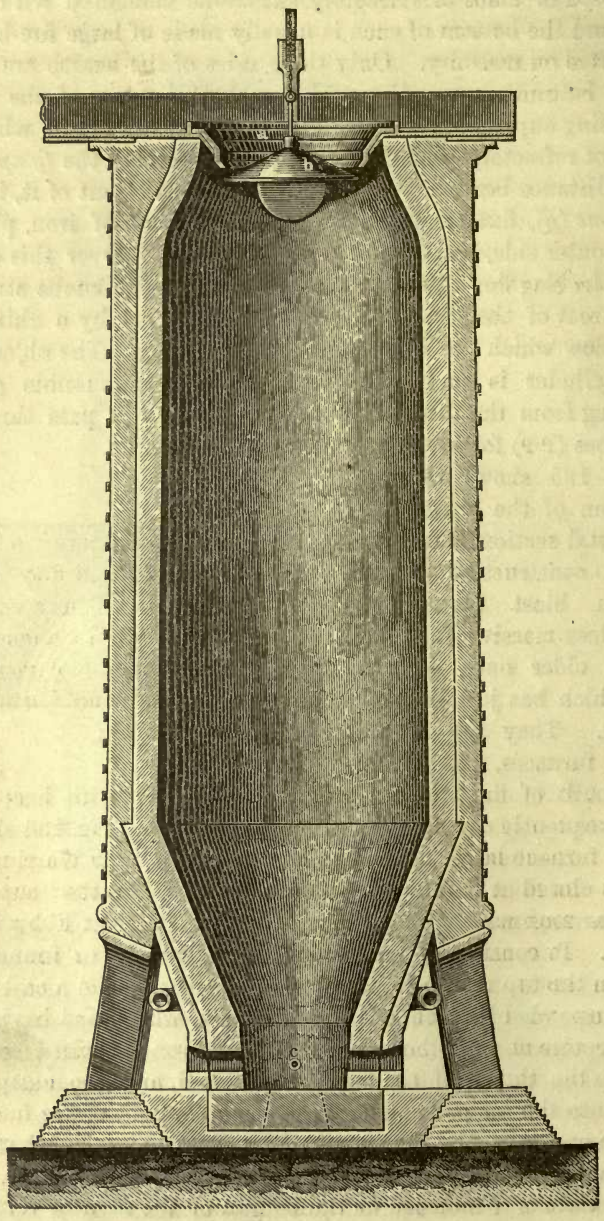


FIG. 136.

in number from two to twelve according to the size of the

furnace. The arrangement of the tuyère pipes, and the construction of the base of the furnace are shown in Fig. 137.

Fig. 138 represents the elevation and section of a blast-furnace which has recently been erected by the Barrow Hæmatite Steel Company. The shaft is 64 feet in height, and is coated with boiler-plate. The cone (*b*) and the cup (*a*) arrangement at the throat enables the charge to be introduced without the escape of the gases. These latter pass through an opening in the side

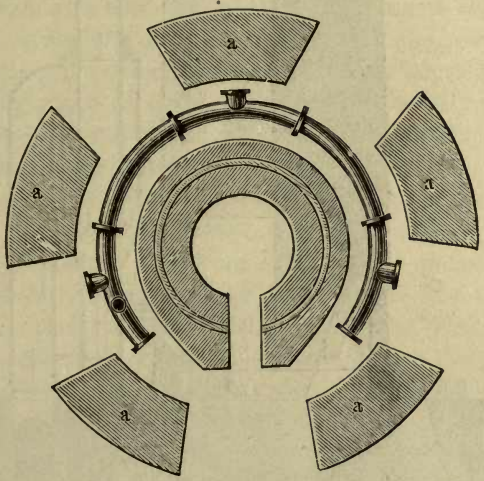


Fig. 137.

of the furnace as shown by the arrows, the gases being drawn upwards at (H), where the dust collects, and then passing into the gas-flue (K). Fig. 139 shows the construction of the furnace in the line (C D); and Fig. 140 that in the line (A B). The former exhibits the five tuyères (*c*) and the main (M) through which the blast is carried.

348 *Hot and Cold Blast.* Up to the year 1828 air was blown into the furnace at the ordinary atmospheric temperature, but in that year J. B. Neilson [1] patented a process for heating the air before it passed into the forge or furnace, and this process, inasmuch as it saved from 15 to 45 per cent. of the fuel, and was also accompanied by an increased productive power of the furnace, was soon generally adopted. For the purpose of heating the air, the waste gases from the furnace are burned in a

[1] Patent No. 5701, March 3rd, 1828.

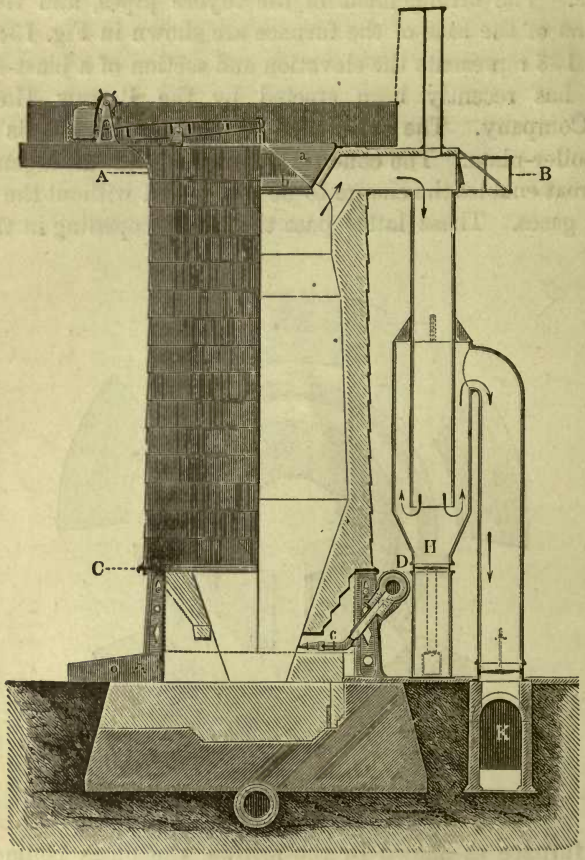


FIG. 138.

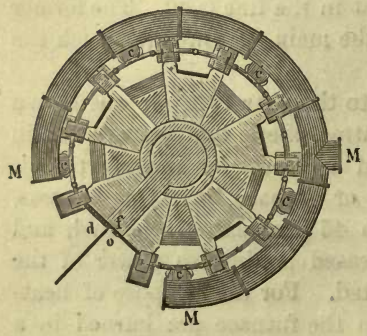


FIG. 139.

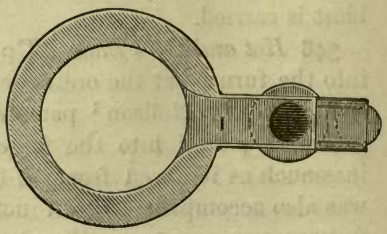


FIG. 140.

Cowper's or Whitwell's stove, which acts on the principle of Siemens' regenerator, and the temperature of the blast raised to a temperature of from 350° to 700°.

The size and shape of blast furnaces have been and continue to be very different. When charcoal is employed, as was formerly universally the case, and is still so in countries where wood is plentiful, the furnace is usually only from 20 to 30 feet in height. The charcoal iron which is thus manufactured in Sweden, Russia, and America is especially valuable for the preparation of fine iron wire, and of the best kinds of steel. Blast furnaces in which the fuel used is either coke, anthracite, or ordinary coal, are, on the other hand, of much larger dimensions, the exact height and capacity of the furnace being regulated by the nature and amount of iron which has to be produced, as well as (it may be added) by the ideas of the ironmaster.

In the year 1750 each English blast-furnace produced about 300 tons of pig-iron per annum, whereas a large-size modern furnace yields about 24,000 tons in the same period. In the Cleveland district, where the blast-furnaces are unusually large, the average capacity of those built up to the year 1854 was about 7,000 cubic feet, whilst those built during the years 1870 and 1871 have an average capacity close upon 30,000 cubic feet, the largest one being that built by Mr. Cochrane, having a height of 92 feet, and a capacity of 42,500 cubic feet. The production of a blast-furnace increases, of course, with its size, but not in a direct ratio; thus Mr. Lowthian Bell has shown that an old furnace of 1853, having a capacity of 6,000 cubic feet, yields one ton of iron per twenty-four hours for every 190 cubic feet of space, whilst in the high furnace built in 1870, 380 cubic feet of space are required to produce one ton of iron in the same time: hence the maximum limit of economic action may be passed by increased size. At the present day somewhat smaller furnaces are again being built.

349 *Blowing-in the Furnace.* For the purpose of starting the newly-built blast-furnace it is necessary that the whole should be gently heated by means of a small fire, usually made by piling a quantity of rough dry timber in the hearth, on to the top of which charges of coke are placed. As soon as the shaft has become warm, regular charges of calcined iron-stone, limestone, and coke are added, until the furnace is filled. The blast is then turned on to about one-fifth of the quantity usually employed, the size of the tuyères being so gradually increased that

it is not until the furnace has been in blow for from four to five weeks that the full-sized pipes are used. The proportion of the materials employed, viz., iron-ore, limestone, and fuel, termed the *charge* or *burden*, varies considerably according to the nature of the ore. If it be siliceous or clayey, the proportion of lime added must be increased; whilst if the ore contain lime instead of silica, the addition of silicates may be requisite. The object of these additions is to form fusible slags, which surround the finely-divided and spongy metal formed during the first stages of the operation, and thus preserve it from oxidation, at the same time preventing the formation of ferruginous slags and a consequent loss of metal. If more difficultly reducible ores are employed, a less fusible slag is needed. When the furnace is in regular blast, a constant stream of slag passes out from the slag-hole, the iron collecting in the lower part of the hearth, and being from time to time removed by piercing a plug of sand and clay by which the tap-hole has been closed. As soon as the proper proportions between the fuel, ore, and limestone has been ascertained, it is of the greatest importance that these proportions should be strictly adhered to, and for this purpose the charges are regularly weighed, and supplied in alternate layers at the top of the furnace.

Whilst the workman termed the "filler" is occupied in bringing the requisite materials into the furnace, the "stove-man" is employed at the bottom of the furnace; his business is to see that the slag runs regularly over the damstone, and to tap the molten iron at given intervals. Before tapping, the stove-man prepares moulds for holding the metal; these are formed in the sand as a series of parallel trenches, which are placed in communication with the tap-hole. The blast of air is then shut off, and the tap-hole opened by piercing the plug with a long bar of iron. The melted iron flows into the channels communicating with the moulds and assumes the form of semi-cylindrical bars or pigs united to one another by one of larger dimensions termed the sow.

If, owing to some accident to the machinery, a blast-furnace is obliged to stand when hot, the operations may be suspended for several days if the throat and tuyère-holes be closed up with sand or clay. Should, however, serious damage have occurred, the furnace must be "blown out." This is accomplished by reducing the burden, and thus increasing the temperature for a time so as to remove any aggregations of solid

matters which are fusible only at a high temperature. The contents of the furnace are then allowed to burn out, and the last tapping is made at a point as low down in the hearth as possible. The life of a blast-furnace varies considerably, lasting from two to twenty years or even for a longer time, according to circumstances.

350 *Chemical Changes in the Furnace.* A large number of investigations have been made on the subject of the chemical changes which occur in the blast-furnace, but in spite of these our knowledge of this subject is still far from complete. The fuel uniting with the oxygen of the blast burns with formation, in the first place, of carbon dioxide, and this is reduced to carbon monoxide by contact with glowing carbon. This latter gas coming into contact with the constantly descending charges of ore, reduces the ferric oxide to spongy metal, and this soon becomes coated with a fusible slag of silicate of lime. The zone in which this reduction occurs is situated at a higher or a lower part of the furnace according to the nature of the ore, and its temperature varies from 600° to 900°. When the ores are porous, they are more easily permeated by the carbon monoxide present, and the reduction takes place more quickly than when denser ores are employed. As the spongy iron descends, it arrives at the hotter parts of the furnace, the temperature of which reaches to 1000° in the belly or widest part of the furnace. At this point the finely-divided spongy iron begins to take up carbon, and it may, therefore, be termed "the zone of carburisation." The iron does not, however, become saturated with carbon until a lower point has been reached, at which the temperature rises to about 1400°. In this zone, which is the hottest part of the furnace, the materials, which were formerly in a pasty state, melt completely, running down into the hearth, where the lighter slag floats on the surface of the heavier iron, and thus protects it from the oxidising action of the blast. Other important changes in the composition of the iron occur as the metal passes down the furnace. In the first place, the spongy iron, in passing through the zone of reduction, takes up sulphur from the ores; and, secondly, when the temperature reaches a higher point in the zone of carburisation, the phosphates contained in the ore are reduced, and the phosphorus is taken up by the iron. At a still higher temperature the fused iron reduces silicon from the silicates, and this, together with manganese, aluminium, and other metals, remains as impurity

in the cast-iron. These various zones of the blast-furnace are not well defined, but pass gradually from one to the other.

351 *Gases of the Blast-Furnace.* The composition of the blast-furnace gases naturally varies in the different zones and under different conditions of burden. The interaction of the carbon dioxide and carbon monoxide present in the blast-furnace gases is of interest. The monoxide is reconverted during the reaction into the dioxide, and this either remains unaltered or is reconverted into the monoxide according to the temperature which prevails in the upper part of the furnace. The researches of Lowthian Bell and von Tunner have shown that the relation between the volumes of the escaping carbon dioxide and carbon monoxide represents, under otherwise similar conditions, the economical working of the blast-furnace, and the limit of economical working is reached when from 40 to 60 volumes of carbon dioxide are present for 100 volumes of carbon monoxide. The furnace gases contain, in addition, nitrogen of the air, hydrogen derived from the reduction of aqueous vapour, as well as hydrocarbons, and frequently small traces of cyanogen.

It has been stated, although there is considerable doubt on the question, that the carburisation of the iron is brought about less by the action of these carbonaceous gases than by the vapours of the cyanides of the alkali-metals, the formation of which can be readily understood when we remember that the ores and limestone always contain alkalis. The finely-divided solid carbon also appears to play an important part in the reduction of the metal, and, according to the experiments of Cailletet,[1] it appears that even at the hottest part of the furnace, and at the point at which the combustion is most perfect, carbon exists in the solid state from the dissociation of carbon monoxide into carbon dioxide and carbon brought about at very high temperatures.

Many analyses of the blast-furnace gases, collected at various heights above the tuyères and under varying circumstances, have been made by several chemists. The following analyses give an idea of the varying nature of the composition of these gases:

[1] *Comptes Rend.* lxii. 891.

Wood-Charcoal Furnace at Veckerhagen, near Cassel. Height 5·97 m. (Bunsen).

Depth in meters below the mouth—	0·86	2·59	4·32
Nitrogen	62·34	63·89	64·58
Carbon dioxide	8·77	3·60	5·97
Carbon monoxide	24·20	29·27	26·51
Marsh gas	3·36	1·07	1·88
Hydrogen	1·33	2·17	1·06
	100·00	100·00	100·00

Hot-blast Coke-furnace at Seraing in Belgium. Height 14·43 m. (Ebelmen).

Depth in meters below the mouth—	0·30	3·05	13·71
Nitrogen	57·06	61·67	54·63
Carbon dioxide	11.39	1·08	
Carbon monoxide	28·61	35·20	45·05
Marsh gas	0·20	0·33	0·07
Hydrogen	2·74	1·72	0·25
	100·00	100·00	100·00

Cold-blast Coal-furnace at Alfreton. Height 11 m. (Bunsen and Playfair).

Depth in meters below mouth—	1·52	5·18	10·36.
Nitrogen	55·35	55·49	58·05
Carbon dioxide	7·77	12·43	
Carbon monoxide	25·97	18·77	37·43
Marsh gas	3·75	4·31	
Hydrogen	6·73	7·62	3·18
Olefiant gas	0·43	1·38	
Cyanogen	—	—	1·34
	100·00	100·00	100·00

Amongst the products of the blast-furnace a variety of substances occur which choke or block up portions of the furnace. Thus in smelting zinciferous iron-ores a compact incrustation of furnace-calamine, consisting chiefly of oxide of zinc, is found round the throat of the furnace, and no less than 100 tons of this compound, termed "gichtschwamm," are annually obtained from iron furnaces near Aix-la-Chapelle.

An interesting substance sometimes found in the blast-furnace is a cyano-nitride of titanium; and, in addition to this, "kish," or graphite, as well as silicates, sulphides, and the oxides of other metals, occur as solid deposits in the furnace.

352 *Varieties of Pig- or Cast-Iron.* Pig-iron may be divided into two chief classes, *white cast-iron* and *grey cast-iron*, and between these we have several intermediate conditions classed together as *mottled cast-irons.*

White cast-iron contains the whole of its carbon in the combined state, and when the iron is dissolved in hydrochloric or sulphuric acid various hydrocarbons are formed, and these impart a peculiar and disagreeable odour to the hydrogen which is evolved. Grey cast-iron, on the other hand, in addition to chemically-combined carbon, contains graphite, and this separates out as black scales when the iron is treated with an acid. This fact was known to Bergman, whilst Guyton de Morveau proved that cast-iron is formed when wrought-iron is ignited with diamond powder; and Karsten showed that cast-iron contains carbon both in the combined state and free in the form of graphite, this latter remaining behind when the iron is dissolved in an acid. The graphite can also be mechanically separated from the iron by sieving (Snelus).

White cast-iron, of which Spiegeleisen is a variety, can generally be produced more cheaply than grey, and is formed when the burden of the furnace is heavy and the temperature comparatively low. It melts at a lower temperature than grey-iron; it is less liquid, and on cooling passes through an intermediate or pasty state, contracting considerably on solidification. Grey cast-iron, on the other hand, is formed at a high temperature and expands on solidification, and is for this reason best adapted for foundry purposes.

Spiegel or specular pig-iron is a white-iron containing the largest proportion of carbon, varying from 3·5 to 6 per cent. It is extremely hard and highly crystalline, and contains manganese as an essential constituent. The specific gravity of spiegel is from 7·6 to 7·7, and it is largely used in the manufacture of steel. When spiegel contains 25 per cent. and upwards of manganese, the mass attains a granular structure, and is termed *ferro-manganese.* It is largely employed in the manufacture of steel by the Bessemer process.

The following analyses give the composition of spiegel and ferro-manganese:

	Spiegel.				Ferro-manganese.	
Locality.	Dannemora.	Siegen.	Duisburg.	New Jersey.	Prieger.	Seraing.
Iron . .	92·906	88·56	76·030	81·863	10·14	51·98
Manganese.	1·987	5·75	18·700	11·500	72·75	40·45
Carbon . .	0·809	5·04	4·770	6·900	7·15	5·44
Silicon . .	0·176	0·41	0·090	0·100	0·87	1·86
Sulphur .	trace	0·08	0·012	0·137	0·02	0·21
Phosphorus	0·122	—	0·280	—	0·07	0·10
Copper . .	—	0·16	0·118			
	100·000	100·00	100·000	100·000	100·00	100·00

The slags of spiegel are rich in manganese and calcium.

353 *White-Iron.* This contains less carbon than spiegel, and is formed when the temperature of the furnace is not high enough for complete carburisation. It melts at a higher temperature than spiegel, and when heated it remains for some time in a pasty condition before fusing completely. White-iron is very hard and brittle, it possesses a laminar structure, and is sometimes vesicular or honey-combed from the evolution of gas given off as the metal cools. It is especially used for the preparation of wrought-iron. Its composition is seen from the following analyses:

Analyses of White-Iron.

Locality.	Durham.	Gartsherrie.	South Wales.	Eisenerz.	Neuberg.	Luxemburg.	Schwechat.
Iron . .	93·183	89·41	94·40	96·189	94·205	94·87	93·711
Manganese	2·370	2·71	0·20	0·453	1·820	0·22	2·670
Carbon . .	4·100	3·33	2·40	3·009	3·123	2·10	2·830
Silicon . .	0·230	1·12	0·80	0·265	0·616	0·91	0·520
Sulphur .	0 030	2·52	0·70	0·011	0·045	0·08	0·085
Phosphorus	0·073	0·91	1·50	0·073	0·036	1·82	0·184
Copper . .	0·014	—	—	—	0·155		
	100·000	100·00	100·00	100·060	100·000	100·00	100·000

The slags of white-iron contain less calcium than those of spiegel.

Grey-Iron. When the temperature of the furnace is high the iron contained in the furnace above the zone of fusion becomes saturated with carbon and grey-iron is formed, from which a part of the carbon separates out on cooling in the form of crystalline scales of graphite. Grey-iron is a mixture of white iron with a crystalline iron free from carbon. It possesses

a lighter or a darker colour according to the quantity of graphite which separates out, and several intermediate qualities of *mottled cast-irons* exist between white- and grey-iron, these being produced when the temperature does not greatly exceed that necessary for carburisation. If molten grey pig-iron be quickly cooled by running into water or into a cold metal mould chilled white iron is produced. This possesses a scaly crystalline structure and a white colour, and contains very finely-divided graphite in addition to combined carbon. On the other hand, if white iron be slowly cooled from the fused state it is converted into grey-iron.

354 *Mottled-Iron.* This variety of cast-iron stands in an intermediate position between white- and grey-iron. It is obtained from pure but difficultly reducible ores worked at a temperature so high that a homogeneous product is formed which does not contain an excess of either graphite or silicon. Such iron has a light grey granular structure, and can be used both for the foundry and for the production of wrought-iron, as well as for the production of Bessemer steel.

Analyses of Mottled-Iron.

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)
Iron	93·691	—	94·45	93·301	92·74	94·56	88·89
Graphite . . .	3.768	1·86	2·28	2·930	4·40	3·10	2·59
Combined Carbon	0·532	0·35	0·72	0·618	trace	0·04	0·79
Silicon	0·432	2·63	1·35	2·720	2·68	2·16	5·13
Sulphur	0·151	0·10	0·03	0·062	0·08	0·11	0·17
Phosphorus . .	trace	0·03	1·17	0·039	0·10	0·63	1·12
Manganese . .	1·426	0·07	—	0·105	—	0·50	0·77
	100·000	100·00	100·00		100·00	101·10	
		Copper . . .		0·010		Calcium .	0·22
		Nickel and Cobalt		0·049		Magnesium	0·06
		Arsenic . . .		0·075		Titanium .	0·26
		Calcium . . .		0·087			100·00
				99·996			

(*a*) Charcoal iron from Ilsenburg.
(*b*) Coke. Hot blast from Whitehaven.
(*c*) „ „ „ Cleveland.
(*d*) Bessemer pig, from Crown point, Lake Champlain.
(*e*) Hot blast from Scotland.
(*f*) Coke. Cold blast from Dowlais.
(*g*) Silvery iron, Clarence.

If pure ores and pure fuels are smelted with cold-blast and suitable burden, a light grey iron is obtained containing little silicon, and valuable for the manufacture of the best wrought-

iron for the production of fine wire; whereas when the temperature of the blast is high, and when common ores containing sulphur are employed, a granular iron suitable for foundry purposes is obtained. If the ore be rich in clay and silicates, a light finely-granular iron known as *silvery-iron* is produced under the latter conditions as regards temperature.

(III.) Production of Wrought-Iron from Cast-Iron.

355 Wrought-iron contains less than 0·5 per cent. of carbon, and its malleability increases as the quantity of carbon diminishes, whilst its point of fusion rises. Wrought-iron is malleable, and at a strong red-heat becomes plastic so as to be capable of being welded, and this the more readily the lower its percentage of carbon. Malleable iron containing only small quantities of carbon, retains its hardness under all circumstances, whereas a product containing more carbon, to which the name of *steel* is given, can be hardened or tempered. No sharp distinction can, however, be drawn between wrought-iron and steel, the one gradually passing into the other according to the amount of carbon which the metal contains.

It has already been stated that before the introduction of the blast-furnace malleable iron was obtained on a small scale by direct reduction from the ore. But gradual improvements in the iron-manufacture have led to the discovery of a method by which wrought-iron can be obtained in quantities larger than is possible by the old bloomery processes. This consists in the conversion of cast-iron into wrought-iron.

The first step in this conversion is termed *refining*. It consists in the fusion of the pig in an oxidising atmosphere in a refining furnace heated by a blast, the object of the operation being to oxidise the carbon and silicon contained in the cast-iron. The processes adopted for this purpose vary considerably according to the composition of the iron. Figs. 141 and 142 show the elevation and plan of a six-tuyèred refinery. When the oxidation has proceeded far enough to reduce the percentage of silicon and carbon to the requisite point, the tap-hole is opened and the iron allowed to run into moulds, and the cast-iron cooled by water. The refined iron is highly crystalline, white, and brittle, the carbon being contained in the combined state. The following analyses by Abel of pig-iron, before and after refining, from Königshütte in Silesia, give the different percentages of silicon,

phosphorus, and sulphur, and show that in this process the

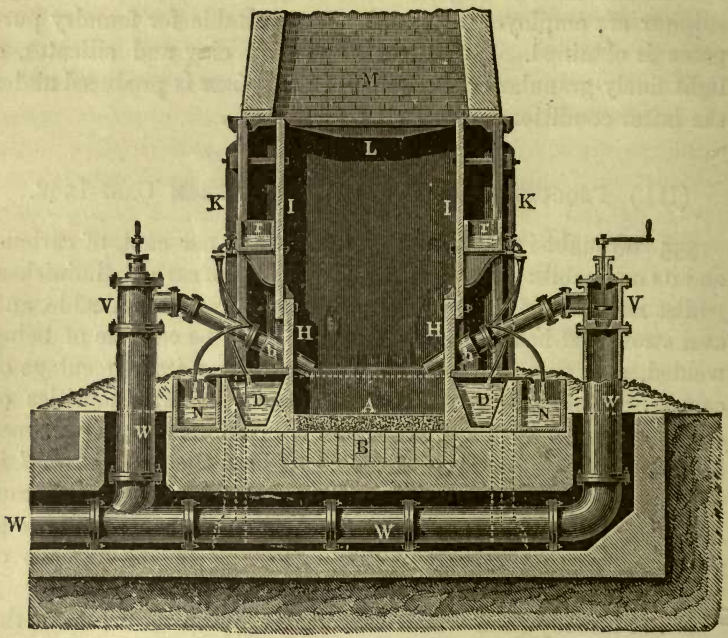


Fig. 141.

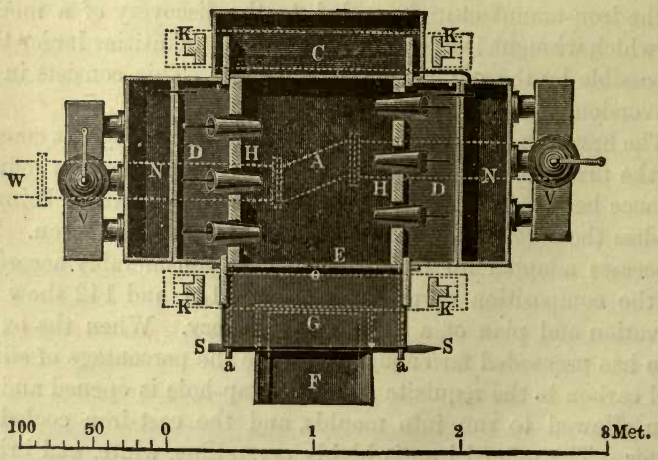


Fig. 142.

silicon is eliminated, whilst phosphorus and sulphur are less affected:

	Pig-iron.	Refined-iron.
Silicon	4·66	0·62
Phosphorus	0·56	0·52
Sulphur	0·04	0·03

The slag obtained in this process, known as *refinery-slag*, forms, when cold, a dark crystalline mass, with an almost metallic lustre. It consists chiefly of Fe_2SiO_4, in which, however, a part of the iron may be replaced by manganese, calcium, magnesium, &c. Not unfrequently distinct crystals of olivine, $(MgFe)_2SiO_4$, have been found.

The refined iron is now ready for its conversion into wrought-iron. This is effected either in an open hearth by a blast of air, a process termed *fining* (the "frischen" of the Germans), or, more commonly, in a reverberatory furnace, when the process is termed *puddling*.

Various methods of fining are in use. Amongst the most important are the German or Wallon, and the Lancashire and South Wales processes. In all of these the pig- or refined-iron is first gradually oxidised, and then worked into a bloom, when the iron is said to "come to nature," and this is afterwards "shingled" or hammered under a "tilt-hammer" into a square block, which can be cut up and rolled into bar.

356 *The Puddling Process.* In England at present the preliminary process of refining has generally been superseded by what is termed "pig-boiling;" that is, the pig-iron is at once submitted to the operation of puddling without previous refining. The chemical reactions which take place in both of these methods are identical. They consist, in the first place, of the conversion of the graphitic into combined carbon, and the consequent change from grey- to white-iron, and afterwards of an almost complete oxidation of the carbon and silicon, whilst in the puddling process the sulphur and phosphorus also are almost entirely got rid of.

The puddling process invented by Henry Cort in the year 1784 is now universally employed wherever fuel is plentiful, as by its means much larger blooms can be worked than is possible in the refinery. An ordinary puddling furnace is shown in elevation, section, and plan in Figs. 143, 144, and 145. The bed or hearth of the furnace (*h*) is supported by a cast-iron plate; at each end of the hearth, which is usually 6 feet long, is a wall built of firebrick, one end being called the fire-bridge (*b*), and the

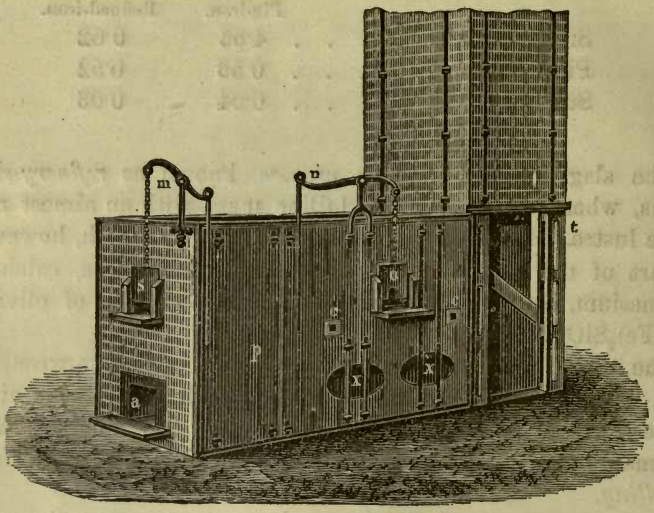


FIG. 143.

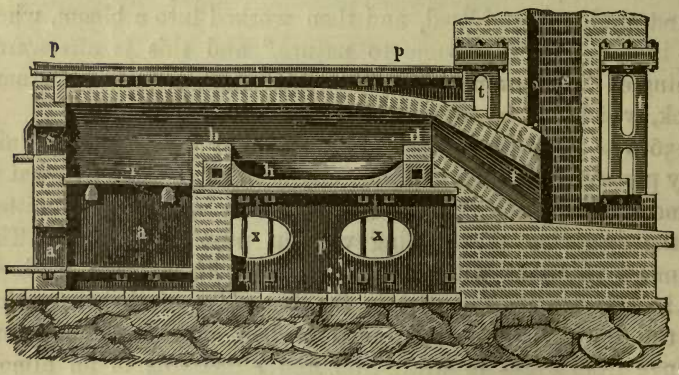


FIG. 144.

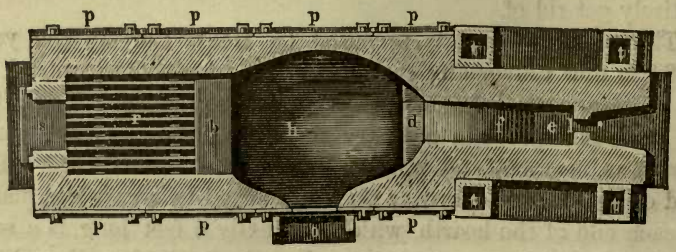


FIG. 145.

other the flue-bridge (*d*). The bottom and side plates of the hearth are lined with a coating of tap-cinder, which is heated until it becomes soft, and is then spread evenly over the floor of the hearth. Above this is placed a coating or "fettling" of ferric oxide of about 1½ inches in thickness, and this is renewed from time to time as it wears away. Neither of these coatings is shown in the figures. The fire-bars, which are sometimes placed in a slanting position, are seen at (F), and the area of the grate should be from one-half to one-third of that of the bed. A powerful draught is obtained by means of a brick chimney, the top of which is furnished with a damper, which can be opened and shut at will by the workman by means of a handle, and thus the passage of air through the furnace regulated. In some furnaces gas is employed with a Siemens' regenerator, and in America, petroleum, or even the gas from the petroleum springs, has been used as a source of heat.

The puddling process may be divided into four stages:

1. The fusion or melting down of the charge.
2. The working-up or incorporation of the fused mass with the oxidising fluxes formed by the union of the iron oxide of the fettling with the silicon, &c., of the cast-iron.
3. The separation of carbon, silicon, phosphorus, and sulphur, and other impurities by exposure to heated air.
4. The mechanical squeezing and hammering of the bloom to get rid of the fusible slag, and to weld the porous iron together to a firm homogeneous mass.

In the puddling, as well as in the refining process, the silicon is first burnt out, and then the carbon gradually disappears. Almost the whole of the phosphorus contained in the pig is found in the *tap-cinder* as phosphide and phosphate. A part of the sulphur probably passes away as sulphur dioxide, but some is left in the cinder as iron sulphide. The tap-cinder is rich in iron, and is difficultly reducible; but it is nevertheless employed for the manufacture of a common kind of iron. The following analysis of tap-cinders give an idea of the composition of this material:

Analyses of Tap-Cinder.

SiO_2.	FeO.	MnO.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	P_2O_5.	S.	Analyst.
7·71	66·32	1·29	8·27	1·63	3·91	0·34	8·07	1·78	Riley.
11·76	58·67	0·57	17·00	2·84	2·88	0·29	4·27	3·11	,,
29·60	48·43	1·13	17·11	1·28	0·47	0·35	1·34	1·61	Percy.

357 The following analyses made by J. G. Snelus[1] give an idea of the consecutive chemical changes which take place in the passage from cast- to wrought-iron: (*a*) is the mottled Cleveland iron which was puddled; (*b*) a portion taken out when melted; the composition ten minutes later is shown by (*c*); after a lapse of twenty minutes by analysis (*d*); the composition of the bloom is shown in (*e*); and the puddled bar in (*f*): α C stands for combined carbon, and β C for graphite:

	Fe.	αC.	βC.	Si.	P.	S.	Mn.
a . .	93·19	1·45	1·38	1·24	1·49	0·11	0·63
b . .	95·03	2·83	—	0·82	0·91	0·09	—
c . .	96·46	2·80	—	0·20	0·58	—	—
d . .	98·09	1·17	—	0·05	0·52	—	—
e . .	98·40	0·15	—	0·09	0·45	—	—
f . .	97·13	0·15	—	0·14	0·47	0·04	0·14

Another grey Staffordshire iron (*a*) (Coneygreen) gave the following results: (*b*) is the composition after fusion; five minutes later (*c*); and the composition of the bloom (*d*):

	Fe.	αC.	βC.	Si.	P.	S.	Mn.
a . .	93·29	1·26	1·29	2·25	0·63	0·13	0·91
b . .	95·68	2·55	—	0·92	0·36	0·11	0·43
c . .	96·55	2·50	—	0·27	0·29	0·07	0·18
d . .	95·75	—	—	0·38	0·25	0·05	0·16

This iron was puddled in Danks' revolving furnace, and in consequence of the reduction of iron from the slag, the yield of wrought-iron was from 10 to 12 per cent. in excess of the weight of the pig-iron used, whereas in the ordinary puddling furnace a loss of iron of the above amount is usually met with.

358 *Mechanical Puddling Process.* In order to avoid the heavy mechanical labour necessary in the ordinary puddling processes, revolving puddling furnaces have been invented by Danks, Crampton and others. The construction of these furnaces is somewhat similar to that of the revolving black-ash furnace. The oxidation is entirely effected by the oxide of iron of the "fettling," the carbon and silicon being thus burnt out, and the phosphorus and sulphur removed in the cinder or slag formed. It would seem that the amount of sulphur and phosphorus

[1] *Report Iron and Steel Institute*, 1872, 246.

contained in mechanically puddled iron is less than that present in ordinary puddled bar.

359 *Properties of Wrought Iron.* Good hammered and rolled bar-iron, when it contains from 0·15 to 0·3 per cent. of carbon possesses a fibrous texture, but when the amount rises to 0·5 or above it possesses a granular or crystalline structure. Fibrous iron is soft and possesses a grey colour ; granular iron is harder and has a dead silvery lustre. The hardness of iron increases with the amount of carbon, until when 0·6 per cent. is reached, the metal becomes steel. Iron melts at from 1,900° to 2,100°, according to the amount of carbon which it contains. The physical properties of commercial iron vary widely, being largely influenced by the nature and amount of the impurities which the iron contains. Thus, for instance, sulphur imparts to iron the property of becoming brittle whilst hot, or, as it is technically termed " red-short," whilst phosphorus renders iron weak at the ordinary temperature, when the iron is said to be " cold-short " Cold-short iron exhibits a peculiar fracture, and the property of cold-shortness appears to depend upon a peculiar crystalline condition of the iron, so that it appears probable that the method of manufacture as well as the percentage of phosphorus has an influence in producing the condition of the iron. The lower the temperature at which the puddling takes place the more easily is the phosphorus got rid of. For at a high temperature the iron takes up phosphorus from the phosphates contained in the siliceous slags. This fact has lately been made use of by Mr. Lowthian Bell in a proposal to extract the phosphorus in the process of Bessemer-steel making.

Silicon exerts an influence similar to that of carbon, making the iron harder and more easily fusible. Manganese prevents this action, and, in the puddling process, assists the removal of sulphur and silicon. Copper in a larger proportion than 0·5 per cent. produces red-shortness, and arsenic increases the brittleness and reduces the welding power, as well as the tenacity of the iron.

(IV.) Steel.

360 Both in its chemical composition and in its properties steel holds an intermediate position between cast- and wrought-iron. Like the latter, steel was obtained in early times directly from the ore.

Homer sings—

> And as when armourers temper in the ford,
> The keen-edged pole-axe, or the shining sword,
> The red-hot metal hisses in the lake;
> Thus in his eyeballs hissed the plunging stake."
>
> POPE'S *Odyssey*, book ix.

These remarks evidently apply to steel, as wrought-iron cannot be thus tempered. The Chalybes on the coast of the Black Sea were renowned for their ability in working the iron ores into steel, and the Greek name for steel, χάλυψ, appears to have been derived from the name of this tribe.

The older chemists looked upon steel as a peculiarly pure form of iron, and Basil Valentine, in his *Last Testament*, terms it the "hardest, purest, most malleable iron." Lemery held peculiar views respecting steel. In his *Cours de Chymie*, published in 1675, he says: "Le fer est un métal fort poreux, composé de sel vitriolique, de soulfre et de terre mal lié et digéré ensemble. On le réduit en acier par le moyen des cornes ou des ongles d'animaux, avec lesquelles on le stratifie et ensuite on le calcine; ces matières contenant beaucoup de sel volatile qui est alcali, tuent les acides de fer qui tenoient ses pores ouverts, et les rendent plus compacte."

Stahl considered iron to be an impure metal containing earthy materials, whilst steel was the pure metal saturated with phlogiston. Similar views were held by the later chemists. Bergman was the first to distinguish chemically between wrought-iron, steel, and cast-iron. He found that the first when dissolved in acids yielded the largest quantity of inflammable air, steel somewhat less, whilst cast-iron gave the smallest quantity; hence he concluded that steel contained less phlogiston than wrought-iron. He also showed that cast-iron contains more graphite than steel, and this more than wrought-iron, and hence he concluded that cast-iron is converted into steel by loss of graphite and by absorption of phlogiston, whilst he supposed that when steel is produced from wrought-iron the opposite reactions occur. Rinnman in 1782 developed similar views, and he especially insisted that malleable iron is a perfect metal, and is converted into steel by absorption of phlogiston, but that this phlogiston is not the substance usually thus designated, but plumbago. In 1786 Monge, Vandermonde and Berthollet published a research proving that the difference between the various kinds of iron is mainly determined by the variation in the amount of carbon which they contain, but the many doubtful

points which remained were only cleared up by the comprehensive researches of Karsten and Sefström.[1]

361 Twenty-five years ago the only method by which steel could be made was the decarburisation of the cast-iron in the puddling furnace, and the subsequent re-carburisation of the puddled bar by the cementation process. The product was then either fused in a crucible yielding cast-steel, or drawn out under the hammer, whereby tilt-steel or shear-steel was obtained. We are now acquainted with several methods by which steel can be made directly from cast-iron.

The *cementation* method of preparing cast-steel is mentioned by Agricola in his *de re Metallica*, whilst that of hammered or tilt-steel was first described by Réaumur in 1722.

In the manufacture of steel by the cementation process, carbon is added, probably through the medium of carbon monoxide, to the otherwise pure wrought-iron. This is carried on in the furnace shown in Figs. 146 and 147. Into the furnace are built two

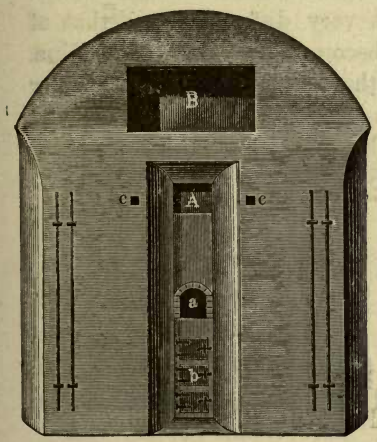


FIG. 146.

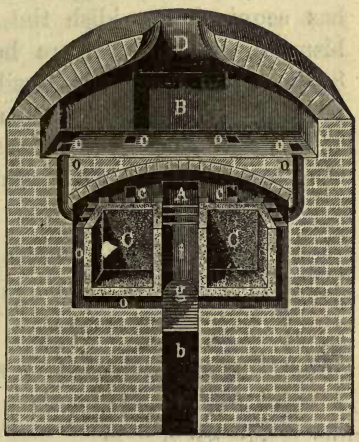


FIG. 147.

square boxes, or "converting pots," c c, Fig. 147, of infusible firebrick; and into these are placed the bars of iron which are to be converted into steel. The flames from a fire placed in the hearth (*g*) play round these boxes. The iron which has to be converted into steel is usually in the form of straight bars about 3 inches (75 mm.) broad, and 0·75 inch (18 mm.) thick, and are somewhat shorter than the converting pot into which they are placed. The

[1] Percy, *Iron and Steel*, p. 116.

interstices between the bars when piled in the pot are filled up with powdered charcoal or soot, technically termed "cementing powder," a thick layer of the charcoal being placed on the top of the bars, and the whole mass plastered over with grinders' waste. The total weight of iron contained in each box is from five to six tons. The fire is gradually raised to a full red-heat, or to about the melting point of copper, and it is maintained at this point for about from seven to ten days, according to the quality of steel which is needed. Spring-steel requires seven days, shear-steel eight days, and steel for welding from nine to ten days. During the operation trial bars are removed by the openings (c) from the ends of the chests, and when it has been found that the bar-iron is completely converted into steel the furnace is allowed to cool, and after several days the charge is removed. The steel bars thus obtained retain the form of the original iron, but in physical properties they differ considerably from the original. Thus the coloured surface of the fractured bar of steel has no longer the bluish tint of malleable iron, but has acquired a reddish tint, not very different from that of bismuth, and the texture has become distinctly crystalline. Steel is also much more fusible than iron, and about 1·5 per cent. of carbon has been taken up.

The following is an analysis by David Forbes of cementation-steel made at Sheffield from Swedish iron:

Combined Carbon.	Graphitic Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
0·627	0·102	0·030	0·005	0·000	0·120

An English cement-steel was found by Berthier to contain 1·87 per cent. of total carbon, and 0·10 per cent. of silicon, the remainder being iron.

A remarkable alteration of the surface is likewise noticed in the passage of wrought-iron into steel, it being covered with blisters or blebs, and hence it is termed *blister-steel*. The formation of these blisters is undoubtedly due to the production of gas within the bar, but what the nature of this gas is is somewhat doubtful. Probably it arises from the combination of a part of the carbon with oxygen derived from particles of oxide of iron contained in the interior of the bar.

362 Various hypotheses have been proposed to account for the phenomena observed in the cementation process. According

to one view, the carbon is absorbed from the exterior and passes to the interior of the bar partly from the solid fuel, partly from the carbon monoxide formed by its partial combustion, and partly from the hydrocarbons derived from the hydrogen contained in the charcoal. The probability of the view that the carbon monoxide is the active agent is strengthened by the fact observed by Graham, that red-hot iron has the power of absorbing from eight to ten times its volume of this gas. Others have assumed that the carburization is brought about rather by the hydrocarbons than carbon monoxide, and that it is especially effected by the vapours of the potassium cyanide, formed by the action of potassium carbonate and carbon, upon the nitrogen contained in the air still left in the boxes, and in support of this hypothesis it is stated that the cement powder loses its power after it has been used for some time and has lost its alkalis. It is also a well-known fact that the cyanides of the alkali metals have the power of giving up carbon to cast-iron.

Cast-steel is obtained by melting blister-steel in plumbago crucibles. This is used for the manufacture of the best kind of cutlery. The commoner variety of cast-steel is now obtained on a very large scale by other processes.

One of these, suggested by Karsten, but first carried out on the large scale by Krupp of Essen, consists in fusing pure wrought-iron with the requisite quantity of spiegel. The progress which has been made in the manufacture of cast-steel by this process is illustrated by the fact that one of Krupp's cast-steel six-pounder guns, exhibited in 1851, was considered a marvel, whilst in 1873 the same firm exhibited in Vienna, a cast-steel block weighing 52,500 kilograms, for the purpose of casting which 1,800 melting-pots, each holding thirty kilos of steel, were employed.

363 *Bessemer Steel Process.* Since the year 1856 a complete revolution has taken place in the iron industry, and this has mainly been caused by the discovery of a method for manufacturing cast-steel from cast-iron. This discovery was made by Mr. Bessemer,[1] and first communicated in a paper read before the Mechanical Section of the British Association, at its Cheltenham meeting, in 1856, and entitled "The manufacture of malleable iron and steel without fuel." The principle upon which this process depends, is, that the heat evolved by the oxidation of the silicon, carbon, and manganese, contained in the molten pig-iron by a current of air

[1] Patent, Dec. 7, 1855. No. 2,768.

blown through the molten metal is sufficient to keep the whole in a liquid state until the cast-iron is converted into steel, this being effected without the intermediate laborious and costly processes of puddling and cementation. The first experiments which were made were unsuccessful, for although by this process the carbon and silicon can be removed, the phosphorus and sulphur which are contained in the pig remain in the finished steel, and for this reason the ordinary impure English cast-iron yielded unsatisfactory results. The case, however, was otherwise when the pure Swedish charcoal-pig was used; indeed the first real success in working the process was achieved with this iron at the Högbo Ironworks, at Sanviken, and this was followed by the successful use of grey-iron made from the Ulverston hæmatite, and now technically known as *Bessemer-pig*. Other difficulties then arose such as the too complete oxidation, when the whole of the carbon is burnt out, a mass of pasty wrought-iron being produced instead of liquid steel. This was overcome by the important suggestion made by Mushet,[1] of the addition of spiegel at the end of the operation in such quantity as is necessary for the conversion of the whole of the wrought-iron into steel.

The oxidation is carried on in an egg-shaped vessel, termed the converter (Figs. 148, 149), made of wrought-iron plates bolted firmly together and lined with an infusible siliceous rock termed gannister which is ground, moistened with water and applied in the form of a paste to the interior. The lower portion is an interchangeable bottom, consisting of a shallow lower section of the vessel with tuyère-box or wind-box and tuyères, together with the necessary arrangements for fixing these in their places. This bottom is attached to the vessel in such a manner that the narrow space between it and the vessel lining may be rammed with plastic gannister by men working outside of the vessel, and this joint can be easily made at once upon pulling away the old bottom. This arrangement is of great advantage, inasmuch as by its use the number of blows per diem can be considerably increased. The pig-iron, which must be free from phosphorus and sulphur, is first melted in a cupola, and from five to twelve tons of this run into the converter, either directly from the cupola or from an intermediate ladle, the mouth of the converter being lowered to the proper angle to receive the molten metal. The converter is then gradually raised to the vertical position; at

[1] Patent, Sept. 22, 1856.

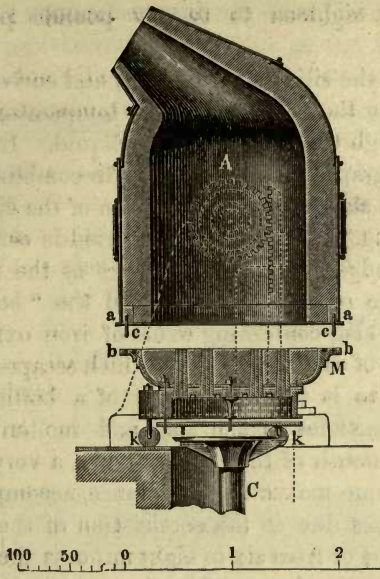


FIG. 148.

the same time a moderate blast of air is thrown through the tuyères by means of the pipes L N and D, and the pressure of the blast is

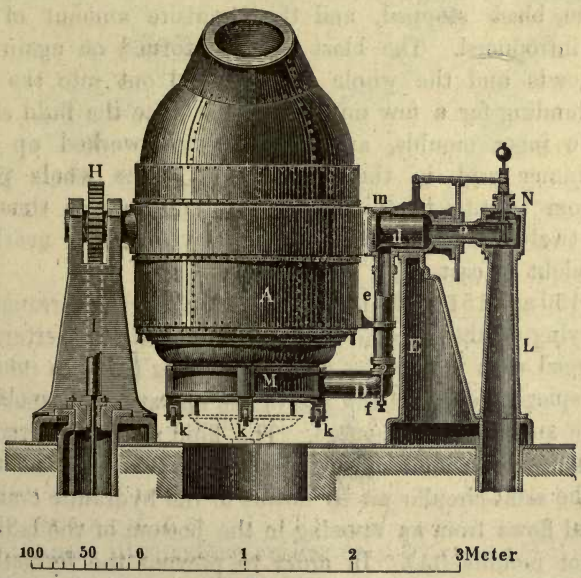


FIG. 149.

then raised to from eighteen to twenty pounds per square inch.

The combustion of the silicon, manganese, and carbon, as also of a portion of the iron then begins, and the temperature rises to a point sufficiently high to keep the metal liquid. In the first part of the blow the graphite is converted into combined carbon and a highly siliceous slag is formed, a portion of the silica being derived from the lining. When the first period is complete an orange-yellow flame edged with blue appears at the mouth of the converter, and the second period termed the "boil" then begins. In this, the slag containing oxide of iron oxidises the carbon, with formation of carbon monoxide which escapes throughout the mass giving to it the appearance of a boiling liquid. During this period particles of the slag and molten iron are thrown out from the mouth of the converter, and a very brightly luminous flickering flame makes its appearance, accompanied by a rapid stream of sparks due to the combustion of the particles of iron. After the lapse of from six to eight minutes the intensity of the action diminishes, the shower of sparks ceases, and suddenly the flame disappears or is said to drop. The whole of the carbon has now been oxidised, and if the blast be left on the combustion is continued at the expense of a portion of the iron. Hence, the force of the blast is now lessened, the converter inclined, then the blast stopped, and the requisite amount of fluid spiegel introduced. The blast is then turned on again for a few seconds and the whole mass poured out into the ladle. After standing for a few minutes in the ladle the fluid steel is cast into ingot moulds, and the cast-steel worked up under the hammer and in the rolling mill. The whole process lasts from twenty to thirty minutes, and in this time from five to twelve tons of cast-iron are converted into nearly the same weight of cast-steel.

Figs. 150 and 151 show the newest English form of arrangement for carrying on the Bessemer process. The two converters (AA), are charged with molten pig from the cupola furnaces (BBB), the molten spiegel needed at the end of the operation being obtained from the smaller furnaces (CC). The fluid steel is poured from the converter into the ladle (G) which can be elevated and carried round the semi-circular pit by means of the hydraulic crane (D). The steel flows from an opening in the bottom of the ladle into the ingot moulds (LL). In order to prevent the formation of bubbles which occur when the steel is run directly into these

moulds, an arrangement (shown at M), is employed by which the liquid metal is allowed to run in at the bottom of the mould.

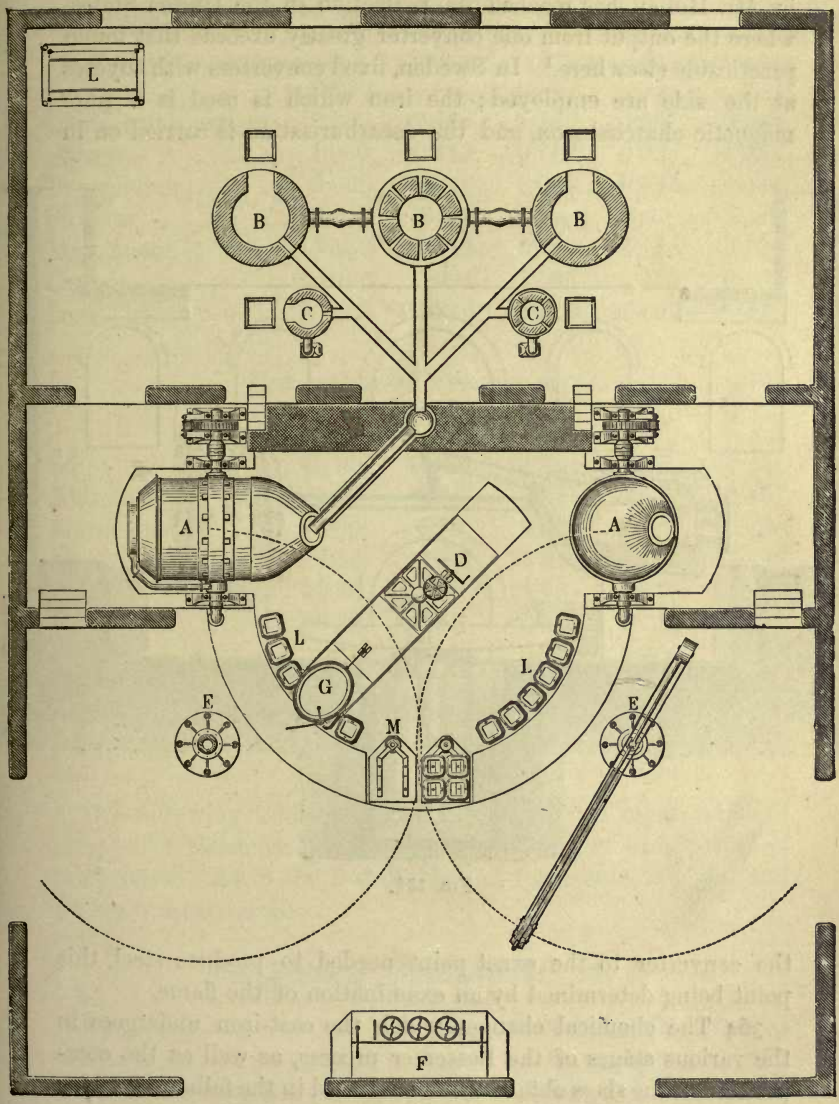


FIG. 150.

The steel-ingots after cooling are removed by means of the long-armed hydraulic cranes (EE), and the whole of the movements of

the converter, ladle and cranes are controlled by the foreman by working the wheels (F).

The arrangement of Bessemer plant, especially that designed by Mr. Holley, has reached its perfection in the United States, where the output from one converter greatly exceeds that found practicable elsewhere.[1] In Sweden, fixed converters with tuyères at the side are employed; the iron which is used is a pure magnetic charcoal iron, and the decarburisation is carried on in

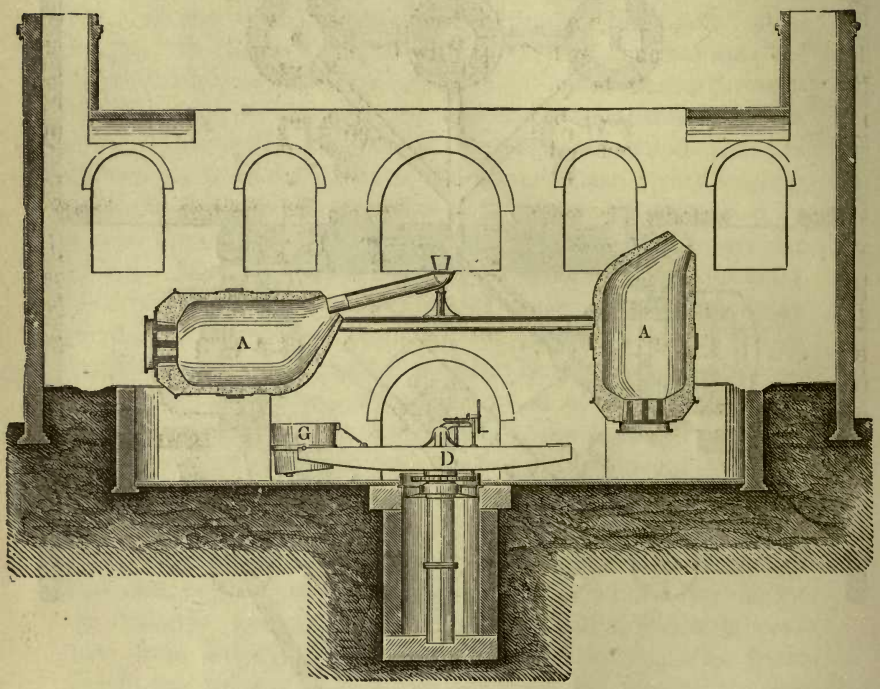


FIG. 151.

the converter to the exact point needed to produce steel, this point being determined by an examination of the flame.

364 The chemical changes which the cast-iron undergoes in the various stages of the Bessemer process, as well as the composition of the slags obtained, are exhibited in the following table:

(*a*) Composition of the pig-iron used (3,517 kilos). (*b*) After the first period of twenty-eight minutes blow. (*c*) After the second period of seven minutes blow. (*d*) After the third period

[1] For complete description, see *Engineering*, March 9 and 16, 1867.

of three minutes blow. (*e*) Finished steel (3,058 kilos) after the addition of 168 kilos of spiegel.

Composition of Bessemer-metal. No. 1.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	3·180	—	—	—	—
Chem. comb. carbon	0·750	2·465	0·909	0·087	0·234
Silicon	1·960	0·443	0·112	0·028	0·033
Phosphorus . . .	0·040	0·040	0·045	0·045	0·044
Sulphur	0·018	Spur	Spur	Spur	Spur
Manganese . . .	3·460	1·645	0·429	0·113	0·139
Copper	0·085	0·091	0·095	0·120	0·105
Iron	90·507	95·316	98·370	99·607	99·445

Composition of Bessemer-slag.

	a.	*b.*	*c.*	*d.*	*e.*
Silica	40·95	46·78	51·75	46·75	47·25
Aluminia	8·70	4·65	2·98	2·80	3·45
Ferrous oxide . .	0·60	6·78	5·50	16·86	15·43
Manganous oxide .	2·18	37·00	37·90	32·23	31·89
Lime	30·36	2·98	1·76	1·19	1·23
Magnesia	16·32	1·53	0·45	0·52	0·61
Potash	0·18	trace	trace	trace	trace
Soda	0·14	trace	trace	trace	trace
Sulphur	0·34	0·04	trace	trace	trace
Phosphorus . . .	0·01	0·03	0·02	0·01	0·01

The following tables contain analyses of two other series of samples of Bessemer-metal, taken at the end of each period of the process. As in the first Table, (*a*) represents the pig, and (*e*) the finished steel.

Composition of Bessemer-metal. No. 2.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	2·519	—	—	—	—
Chem. comb. carbon	1·000	3·040	1·640	0·190	0·370
Silicon	2·260	0·955	0·470	trace	trace
Phosphorus . . .	0·073	0·070	0·070	0·070	0·590
Sulphur	0·107	0·091	0·098	0·093	0·090
Manganese . . .	0·410	—	—	—	0·649

Composition of Bessemer-metal. No. 3.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	2·070	—	—	—	—
Chem. comb. carbon	1·200	2·170	1·550	0·097	0·566
Silicon	1·952	0·759	0·635	0·020	0·030
Phosphorus . . .	0·048	0·051	0·064	0·067	0·055
Sulphur	0·014	Spur	—	—	—
Manganese . . .	0·086	—	—	—	—
Copper	—	—	—	—	0·039

Analyses No. 2 are made by Baker, at the Atlas Works, Sheffield. Analyses No. 3, by Snelus, at Dowlais.

Converter Gases. Snelus has investigated the composition of the gases issuing from the converter. When the charge lasted eighteen minutes he found the following results on analysis of the gases drawn out at the times after the commencement of the blow given in minutes in the first horizontal column:

	2	4	6	10	12	14
CO_2	10·71	8·59	8·20	3·58	2·30	1·3
O	0·92	—	—	—	—	—
CO	—	3·95	4·52	19·59	29·30	31·11
H . . . . . } 88·37	0·88	2·00	2·00	2·16	2·00
N . . . . . }	86·58	85·28	74·83	66·24	65·55

Elimination of Phosphorus. It has hitherto been supposed that the non-elimination of phosphorus in the Bessemer-process is due to high temperature and that if the process could be conducted at a lower temperature, as in puddling, all the phosphorus would be found in the slag. Messrs. Thomas and Gilchrist[1] have, however, lately proved that it is possible completely to eliminate phosphorus in the Bessemer-process by using a lining of lime for the converter instead of the usual siliceous one. They have moreover shown that lime simply added to the contents of the converter also causes the elimination of phosphorus. These observations if confirmed on the large scale, are of the highest possible technical importance.

Application of the Spectroscope to the Examination of the Bessemer Flame. It has already been stated that the point at which the flame drops is that at which it is found by practice to be necessary to stop the blast, but it is not always easy to

[1] *Proceedings of the Iron and Steel Institute*, 1878.

hit this point with accuracy; and if the blow be stopped a few seconds too soon, or carried on for a few seconds too long a time, the quality of the resulting steel suffers. The application of the spectroscope to the determination of this point was made by Roscoe in 1863,[1] and has since been investigated by Watts, Lielegg, Snelus, and others. It appears from these experiments that the point of complete decarburisation can be most exactly and easily determined by the sudden disappearance of certain absorption-bands observed in the spectrum of the flame. These bands, however, are not due in themselves to carbon, but to the presence of the oxides of manganese (Watts), the disappearance of this metal from the molten steel being simultaneous with that of the carbon.

365 *Other Methods of Steel-Making.* Of these that known as the Siemens-Martin process is one of the most important. The steel is produced in a reverberatory furnace by dissolving malleable scrap-iron in molten pig-iron.

Figs. 152, 153, and 154 represent the newest form of a Siemens' 12-ton regenerative steel-melting furnace for producing cast-steel according to the Siemens-Martin process. Fig. 152 gives the vertical section, Fig. 153 the side elevation, and Fig. 154 a transverse section through the line AB Fig. 152. The gases from the producer (see Fig. 123) pass along the iron downcast wrought-iron tube, G and G′, Fig. 153, to the valve V, which can be directed by means of the handles A, so as to pass either into the chamber C or the chamber C′, Fig. 152, where it takes up the heat previously imparted to the bricks by the waste gases. Having thus been heated it passes into the furnace by the flues, meeting with the requisite quantity of air, which has previously been similarly heated by passing through similar chambers, D or D′, and which enters by the upright flues F. The gas and air thus leaving the flues mingle and burn and the flame passes over the hearth of the furnace (*k*), made of infusible sand contained in an iron casing. Supposing that the gas and air are passing through the chambers C and D, the flame plays over the hearth and the heated waste gases find their way through the flues F′ into the chambers C′ and D′, where they heat up the bricks to full whiteness. As soon as this is accomplished, the temperature of C and D being proportionately lowered, the gas valve V, Fig. 153, and the air valve V′, Fig. 154, are reversed, and the currents of gas and air are thus turned into the freshly heated chambers C′ and D′,

[1] *Phil. Mag.* v. 318.

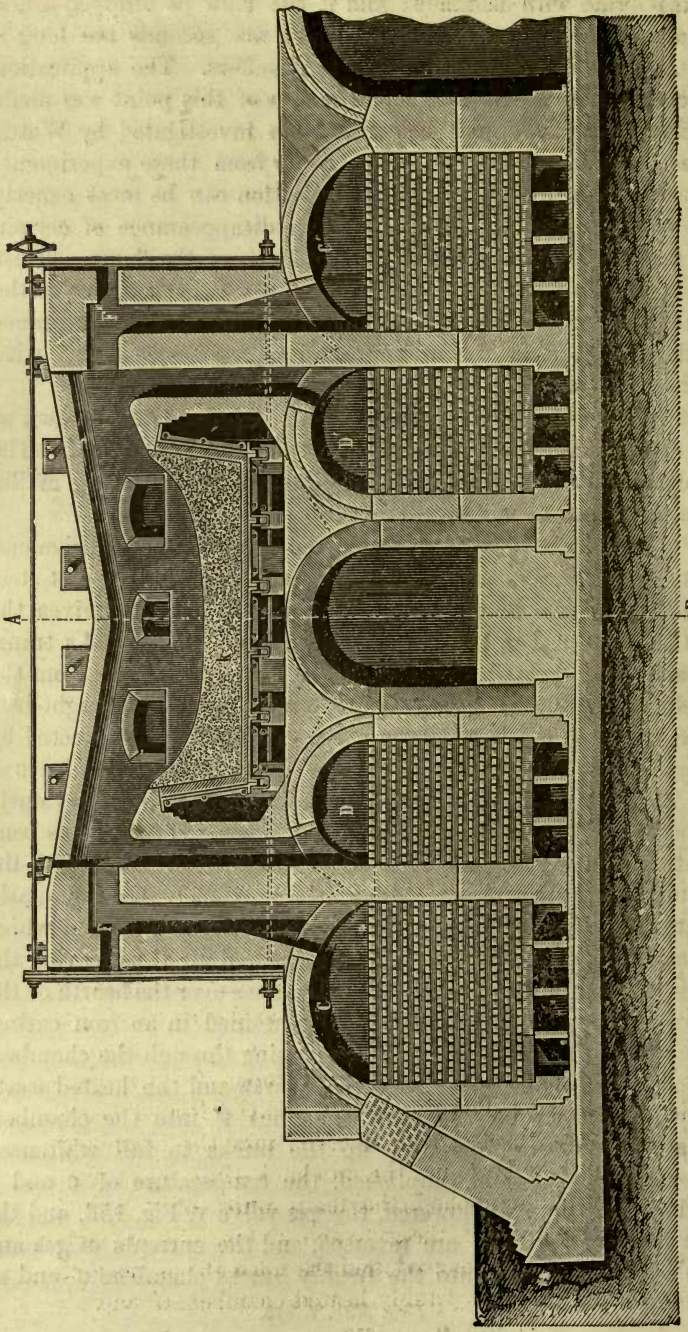


FIG. 152.

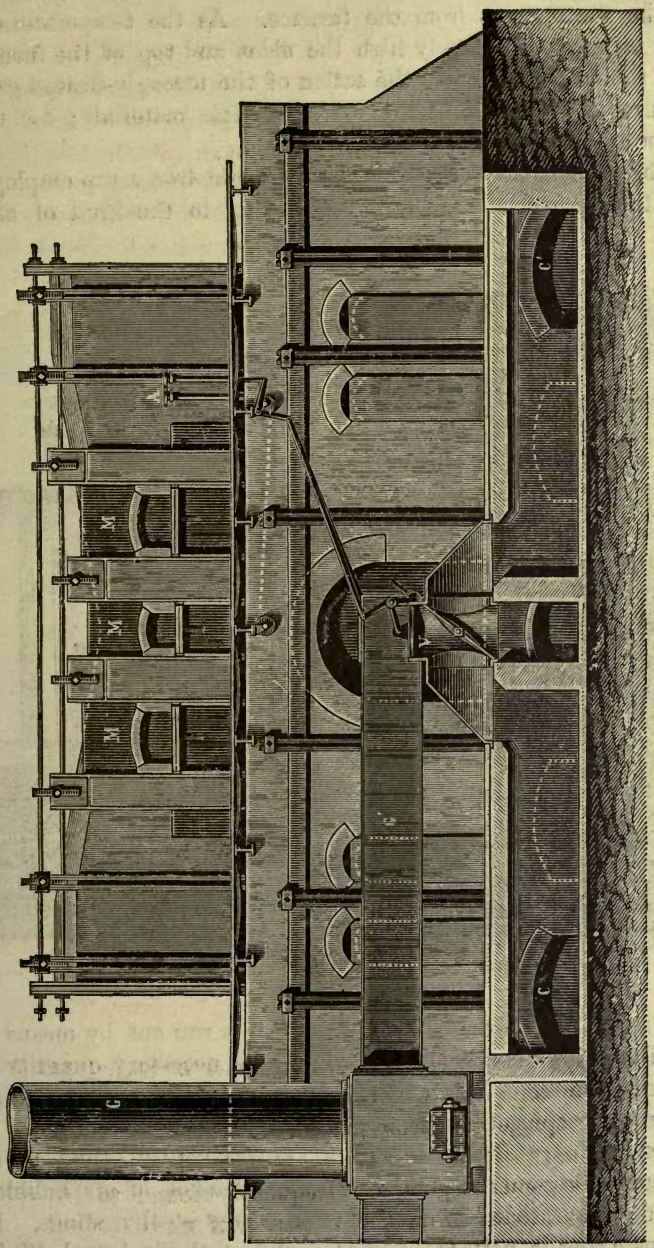


FIG. 153.

whilst the cooled chambers C and D are in their turn heated by the waste gases from the furnace. As the temperature of this furnace is extremely high the sides and top of the furnace and the flues exposed to the action of the strongly-heated gases require to be made of the most infusible materials; for this purpose silica bricks are used.

The proportion of cast-iron and wrought-iron scrap employed for the furnace-charge varies according to the kind of steel

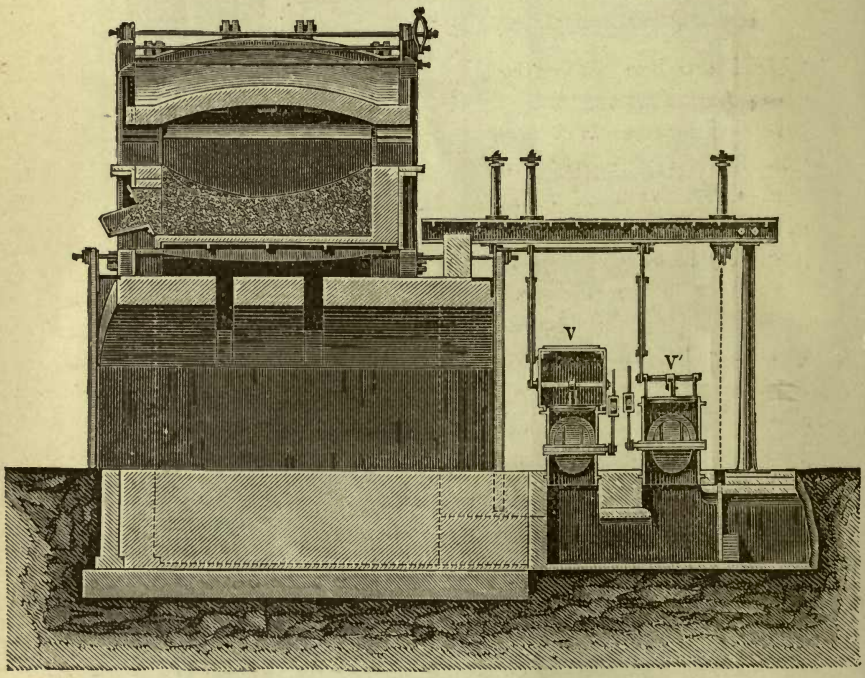


FIG. 154.

required. This, after being well melted, is run out by means of the spout into the ladle into which the necessary quantity of ferro-manganese or spiegel has been placed. The steel is then ready for casting.

The ordinary Bessemer ingots are frequently found to be honeycombed and unsound from the presence of air bubbles, and the same thing is noticed in all large steel castings. In order to obtain perfectly homogeneous steel Sir Joseph Whitworth exposes the molten steel during its solidification to

enormous pressure by means of hydraulic machinery. By this means the metal gains in tensile strength and elasticity as well as in homogeneity.

Pernot's Revolving Hearth.—As the puddling of iron is greatly facilitated by mechanical agitation, an arrangement for effecting a similar agitation in the bath of an open-hearth steel-furnace has been suggested and carried out by Pernot. The general arrangement of the furnace is shown in Fig. 155. It differs from the Siemens-Martin in having a circular hearth supported

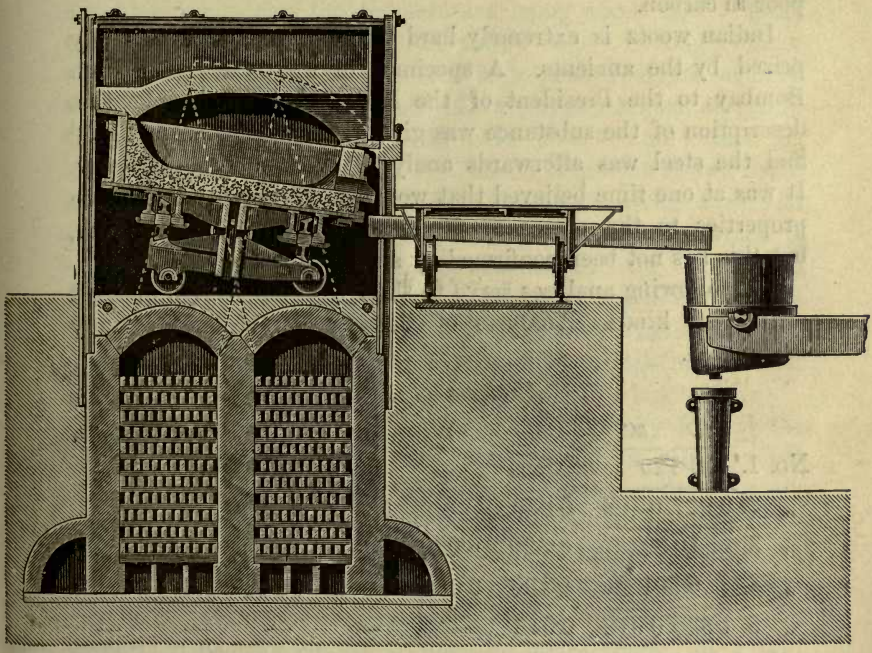


Fig. 155.

on a trolley, by means of which the bottom may be drawn out for re-lining or for other purposes. The hearth revolves on an axis, inclined about 6° to the vertical, thus effecting an intimate mixture of the molten metal, and well exposing it to the action of the flame. The speed of rotation is three revolutions per minute. A hearth for a 10-ton charge is lined up to $8\frac{3}{4}$ feet in diameter, and is 21 inches deep, the arrangement of the regenerators being the same as in the ordinary Siemens. This furnace is largely used in France, and it is claimed that time is

saved and that the steel is more uniform than that made by the ordinary plan. When the process is complete the molten metal is allowed to run into the ladle from which it is passed into the ingot moulds.

Lastly *wootz* or Indian steel must be mentioned. This is a product prepared by heating malleable iron in small clay crucibles, in which small pieces of the wood of *cassia auriculata* are also placed, until the external portions begin to fuse. The product is then hammered frequently and the steel thus consists of a mixture of two irons, one being rich and the other poor in carbon.

Indian wootz is extremely hard and elastic, and was highly prized by the ancients. A specimen of wootz was sent from Bombay to the President of the Royal Society, and the first description of the substance was given by Dr. Pearson in 1795,[1] and the steel was afterwards analysed by Faraday and Henry. It was at one time believed that wootz owed its special valuable properties to the presence of a small quantity of aluminium, but this has not been confirmed by subsequent analysis.

The following analyses serve to show the composition of steel of various kinds. Analyses of Bessemer steel have already been given.

Analyses of Steel.

	αC.	βC.	Si.	P.	S.	Mn.	Cu.	Co & Ni.
No. 1.	1·129		trace	—	trace	—	trace	—
„ 2.	0·627	0·105	0·030	—	0·003	0·120	—	—
„ 3.	1·180		0·330	0·020	—	trace	0·300	0·120
„ 4.	0·501		0·106	0·096	0·002	0·144	—	—
„ 5.	1·336	0·312	0·043	—	—	—	—	—

No. 1. Styrian refinery steel.
No. 2. English cast-steel, from blister-steel.
No. 3. Krupp's cannon steel.
No. 4. English puddled steel.
No. 5. Indian wootz.

366 *Properties of Steel.*—The most characteristic property of steel is its power of assuming an almost adamantine hardness when quickly cooled, as when plunged into water. After this treatment it is extremely brittle, almost perfectly elastic, and so hard that it cannot be attacked by a file. This hardness and brittleness may be partially removed by a process of tempering which consists in heating the steel moderately and then allowing

[1] *Phil. Trans.* 1795, part ii. 322.

it to cool. The temper of steel depends upon the heat to which the steel is raised, and the workman judges as to the temperature by observing the various colours which the surface of the metal assumes during the progress of the operation. The tints thus observed are the colours of thin plates caused by the different thicknesses of the oxide formed on the surface. When the requisite tint is reached the object is quickly cooled. The hardest temper, such as is required for steel for surgical instruments, lancets, and razors, is that obtained at the lowest temperature; the tint employed for this purpose is that first reached, and is of a light straw-colour, the temperature being about 230°. Steel tempered at 243° possesses a full yellow colour, is tougher than the former, and is the tint to which penknives are usually tempered. At 255° a brownish-yellow tint is attained, and steel thus tempered is best fitted for cold chisels and shears for cutting metals. At 265° the first shade of purple shows itself. and this is the temper employed for pocket-knives, axes, and plane-irons. A temperature of 277° gives a purple which is the tint for table-knives and cloth-shears, and for swords and watch-springs, the metal is cooled when it has a bright blue colour, corresponding to a temperature of 288°. At higher temperatures, from 290° to 316°, steel assumes a dark blue colour, and is used for shears, chisels, and especially for large saws.

The different degrees of heat may be attained by dipping the several articles into a bath of fusible metal or oil provided with a thermometer and heated up to the requisite temperature, although in ordinary cases this method is not carried out.

Damascening is produced by repeatedly welding, drawing out, and doubling up a bar composed of a mixture of steel and iron, the surface of which is afterwards treated with an acid. The surface of the iron retains its metallic lustre under the action of the acid, whilst that of the steel is left with a black firmly attached coating of carbon.

Case-hardening is effected by converting the surface of soft iron into steel. Objects of soft iron are heated, together with powdered cast-iron turnings or powdered charcoal, and thus a superficial coating of steel is given to them.

Finely Divided or Reduced Iron (ferrum redactum) has long been used in medicine. *Spongy iron* is now prepared on the large scale by the reduction of burnt pyrites or blue-billy and other ores of iron, and much used as an excellent means of filtering and purifying water for domestic use (Bischof).

IRON AND HYDROGEN.

367 By acting upon anhydrous ferrous iodide with zinc-ethyl $(C_2H_5)_2Zn$, in presence of ether, Carius and Wanklyn obtained, together with zinc iodide, a mixture of gases consisting of ethene, C_2H_4; ethane, C_2H_6; butane, C_4H_{10}; and hydrogen. The residue after washing with ether yields a metallic powder resembling iron which does not undergo any alteration in dry air, but evolves hydrogen on heating, and is decomposed by water with evolution of hydrogen, a residue remaining of metallic iron and ferrous oxide. Hence it would appear that a compound of iron and hydrogen exists which probably has the composition FeH_2. Hydrogen is occluded by electrolytic iron which absorbs thirteen times its volume of this gas (W. Chandler Roberts).

IRON AND OXYGEN.

368 Iron forms two basic oxides,

Iron monoxide, or ferrous oxide, FeO

Iron sesquioxide, or ferric oxide, Fe_2O_3,

and these two unite to form

Magnetic oxide of iron, or ferroso-ferric oxide, Fe_3O_4.

The two latter oxides occur in nature as minerals, and are not only used as ores of iron but are also employed in medicine. Indeed rust of iron (ferric hydroxide) is said to have been used as a medicine by Esculapius, and Dioscorides also mentions *σκωρία σιδήρου*, probably denoting by that iron-scales, as being a substance similar to rust but possessing less active medicinal properties. Red hæmatite was termed blood-stone, and the same author states that this may be obtained artificially by igniting loadstone. Pliny terms iron-rust or scale *squama ferri*, red-iron ore *hæmatites*, and loadstone *magnes*, and describes the action of the latter upon iron. The reddish-yellow and red oxide of iron is called *crocus martis* by Geber. The later chemists describe various methods for its preparation, and in 1735 the artificially prepared black-oxide was termed *œtheops martis*. For a long time these compounds were only distinguished by their different medicinal action. The supporters of the phlogistic theory considered them to be compounds of iron calx

with various proportions of phlogiston. Thus, for instance, Scheele in 1777 states that the precipitate which an alkali produces in a solution of green vitriol when exposed to the air gives rise to crocus martis and that fire-air or oxygen disappears. Hence he concludes that the precipitated calx gives up phlogiston in its conversion into crocus.

Lavoisier distinguished two oxides, æthiops and crocus. Other chemists, like Berthollet, believed that a large number of these oxides exist, and so lately as 1811 the views of chemists on this subject were much divided. Gay-Lussac was the first to point out that in addition to the lower and higher oxide an intermediate compound exists, and this conclusion was confirmed by the investigations of Berzelius.

369 *Iron Monoxide*, or *Ferrous Oxide*, FeO, is obtained as a black powder when hydrogen is passed over the sesquioxide heated to 300°. The product oxidises with incandescence on exposure, but loses this property after it is allowed to remain for twelve hours in an atmosphere of hydrogen (Siewert). When ferrous oxalate, FeC_2O_4, is heated from 150° to 160° in absence of air, a mixture of monoxide and metallic iron is formed, and this is shown by the fact that the gas evolved consists, as Liebig has shown, of fifty-six parts of carbon monoxide and sixty-eight parts of carbon dioxide. If ferrous oxalate is added to boiling caustic potash the monoxide is obtained as a black velvety powder, which when washed with water in the air takes up oxygen (Böttger).

Ferrous Hydroxide, $Fe(OH)_2$, is formed when pure ferrous salt is treated with caustic potash or soda in absence of air. It is a white powder which when freed from air and washed with hot water and ether may be preserved in an atmosphere of hydrogen. As, however, it is difficult to obtain perfect absence of air, the ferrous hydroxide is usually obtained as a green pulverulent mass.[1]

Ferrous hydroxide becomes heated on exposure to air, the mass sometimes becoming incandescent with formation of sesquioxide. It also rapidly absorbs carbon dioxide, and dissolves in acids with evolution of heat. The moist hydroxide also absorbs atmospheric oxygen, changing colour first to a dirty green and afterwards to a brown.

Ferrous hydroxide is formed by the action of pure water, containing air in solution, on iron. It dissolves in about 150,000

[1] G. Schmidt, *Ann. Chem. Pharm.* xxxvi. 101.

parts of water forming an alkaline liquid which possesses the peculiar taste of the ferrous salt.

370 *Magnetic Oxide of Iron*, or *Ferroso-Ferric Oxide*, Fe_3O_4, occurs in large masses as the mineral magnetite. It crystallises in octohedrons, dodecahedrons, and other combinations of the regular system. It has an iron-black colour, and a more or less strong metallic lustre. It frequently occurs in granular or amorphous masses, and is also found in marshes as an earthy mass known as ochreous iron ore (or in German *eisenmulm*). The pure crystallised mineral has a specific gravity of 5·18, whilst that of the granular and earthy material varies considerably, inasmuch as it contains magnesia, lime, titanic oxide, and often contains the iron in a more highly oxidised condition.

The interesting observation that this ore has the power of attracting iron, and that by contact with it iron attains the same polar magnetic properties, was early made. According to some the name is derived from a certain Magnes who was the first to observe this property, whilst according to others the name is derived from Magnesia, a town in Lydia also called Heraclea, where the mineral was first found. The latter explanation would seem to be the more probable, inasmuch as Plato and Theophrastus term magnetite the Heraclean stone. Ferroso-ferric oxide does not always possess the magnetic properties exhibited by loadstone, although attracted by the magnet.

When iron is heated to redness in the air it becomes coated with an iron scale. This is a mixture or a compound of the monoxide and sesquioxide in varying proportions. The inner layer which is blackish-grey, porous, brittle, and attracted by the magnet, has the composition $6FeO + Fe_2O_3$, and is not magnetic. The outer layer contains a larger quantity of ferric oxide, is of a reddish colour, and is more strongly attracted by the magnet than the inner portion. When iron is quickly burnt in oxygen or in the oxy-hydrogen blow-pipe, the magnetic oxide is formed, and the occurrence of this oxide has also been observed in smelting operations.

Magnetic oxide is also obtained when steam or carbon dioxide is passed over red-hot iron, but, on the other hand, when the oxides of iron are heated in a current of hydrogen or of carbon monoxide, they are reduced to metal. When the black oxide is dissolved in hydrochloric acid, or when a mixture in the right proportions of a ferrous and ferric salt is dissolved, and caustic alkali added to the solution, a black precipitate is obtained which dries to a

brownish-black brittle mass giving a dark-brown powder. This hydroxide contains about 7 per cent. of water, and corresponds to the formula $Fe(OH)_2.Fe_2O_3$. It is attracted by the magnet and may in this way be separated from any sesquioxide which may be mixed with it.

371 *Iron Sesquioxide*, or *Ferric Oxide*, Fe_2O_3, is one of the most important ores of iron, occurring as red hæmatite, and as specular iron crystallizing in rhombohedrons and scalenohedrons, possessing a steel-grey colour. It also occurs under the name of micaceous iron in thin red translucent scales. This mineral is found in large quantity and in splendid crystals in the Island of Elba, of which Virgil[1] says: "Insula inexhaustis chalybdum generosa metallis." The crystals have a specific gravity of 5·19 to 5·25.

The mineral martite is also a pure ferric oxide which crystallizes in the same form as magnetic oxide, and is probably a pseudomorph of this mineral. Other more or less pure forms of ferric oxide are red- and yellow-ochre and bole.

Ferric oxide can be prepared artificially in various ways. It is formed by igniting the hydroxide or any ferric salt containing a volatile acid, as a steel-grey crystalline powder, which like all other kinds of sesquioxide of iron, gives a brownish-red powder when finely triturated, and has a specific gravity of 5·17. It may be obtained in small crystals by the action of the vapour of ferric chloride on heated lime (Daubrée), or by fusing ferric oxide and borax together and treating the fused solid mass with hot dilute hydrochloric acid; also by passing a slow steady stream of hydrochloric acid over the strongly ignited oxide (Deville). Artificial micaceous iron is prepared by heating a solution of ferrous sulphate and copper sulphate together for ten hours at a temperature of 210° (Wibel). Ferric oxide has also been observed in the crystalline state as a product in smelting operations, whilst crystals having the form of specular iron, have been found in iron-rust from a building some 700 to 800 years old. The ignited as well as the natural ferric oxide dissolves only slowly in acids, the best solvent being a boiling mixture of eight parts of sulphuric acid and three parts of water. In addition to its use as an iron ore, ferric oxide is of service in a variety of other ways. Thus, the residue left in the process of distilling fuming sulphuric acid from green vitriol (Vol. I. p. 343), termed *colcothar* or *caput mortuum vitrioli*, is used largely as an oil-

[1] *Æn.* x. 173—4.

paint and also as a polishing powder; the least calcined portions, which are of a scarlet colour, are used as jewellers' rouge, whilst the more calcined portions which have a bluish tint are termed *crocus*, and are employed for polishing brass or steel.

372 *Ferric Hydroxide*, $Fe_2(OH)_6$, is prepared by precipitating a moderately dilute solution of ferric chloride with an excess of ammonia in the cold, when a voluminous brown precipitate of the hydroxide is thrown down. The composition of this substance does not undergo change on washing, or on slightly heating, when it forms a dry amorphous granular powder. If the water containing the precipitate be allowed to freeze, a microscopic crystalline powder is formed, and this substance corresponds in composition to the minerals brown-hæmatite and limonite, viz, $Fe_2O_3 + Fe_2(OH)_6$. This hydroxide also exists in nature as ochre, likewise as the deposit of chalybeate waters, the colouring matter of yellow sandstone, &c. Iron-rust has the same composition, as well as the precipitate which is obtained when a ferric salt is precipitated hot, and the precipitate dried over sulphuric acid.

When allowed to remain for a long time in contact with water the hydroxide becomes crystalline, losing thereby the half of its water. The red amorphous compound, $Fe_2O_4H_2 = Fe_2O_3 + H_2O$, is often formed under similar circumstances, and also when a boiling solution of green vitriol is mixed with sodium carbonate and sodium hypochlorite. It occurs as the mineral göthite, having a specific gravity of 4·34. The precipitated ferric hydroxide when heated for some days at a temperature of 100°, forms a scarlet powder $Fe_4O_7H_2 = 2Fe_2O_3 + H_2O$, having a specific gravity of 4·4545, and dissolving with difficulty in nitric acid although more readily in hydrochloric acid. This occurs in nature as the mineral turgite. In addition to these, other hydroxides are known; these are obtained by precipitating the ferric salts under various conditions.

Soluble Ferric Hydroxide. When freshly precipitated ferric hydroxide is added to a solution of ferric chloride, it dissolves to form a basic chloride with production of a dark-red liquid. This may also be obtained by adding ammonium carbonate to a solution of ferric chloride, until the precipitate which is first formed no longer redissolves. If a solution of this kind containing about 5 per cent. of solid constituents be allowed to dialyse for a long time, a dark-red liquid remains which contains only 1·5 per cent. of hydrochloric acid, and 98·5 of ferric oxide. On standing for some weeks this solution gelatinises, a ferric

hydroxide separating out which is readily soluble in cold acids. The same compound may be obtained by the dialysis of ferric acetate, and a liquid thus obtained which only contains six parts of acetic acid to ninety-four parts of oxide of iron. Hydrochloric acid, nitric acid, sugar, and alcohol, do not produce gelatinisation in such a solution, although traces of alkalis and other acids do produce this effect. This soluble hydroxide is used as a medicine under the name of *Liquor Ferri Dialysati.*

373 *Soluble Meta-ferric Hydroxide,* $Fe_2O_4H_2$. This substance was discovered by Péan de St. Gilles.[1] It is formed when solutions of certain iron salts containing monobasic acids are heated for a length of time, and is precipitated from these solutions by the addition of a small trace of sulphuric acid as a brown ochrey powder. It is also obtained in the form of a dark-red powder, by heating well-washed ferric hydroxide with water to a temperature of 100° for from seven to eight hours, and also by heating a solution of basic ferric nitrate for three days to the same temperature. On addition of a few drops of hydrochloric acid the hydroxide is precipitated, and this may be dried on a porous plate where it remains in the form of black scales which dissolve in water, yielding a tasteless red liquid.[2] The same body may be obtained by heating dilute ferric chloride solution and adding common salt; the precipitate which is then thrown down dissolves in pure water, to form a reddish-yellow solution, appearing transparent by transmitted, but opalescent by reflected light.[3]

Meta-ferric hydroxide is insoluble in concentrated, but dissolves in dilute acids, and the solution exhibits the same optical properties as the solution of the meta-hydroxide.

Ferric hydroxide forms a singular compound with sugar, which is soluble in water. This fact is of great importance to the sugar refiners, as this compound destroys the crystallising power of sugar, and therefore increases the quantity of molasses formed. Hence raw sugar ought not to be brought into contact with iron, and the "char" employed for the decolorisation of the sugar should be as free as possible from the compounds of this metal.

374 Ferric oxide combines with several monoxides to form compounds corresponding to ferroso-ferric oxide, all of which resemble this in being magnetic.

[1] *Ann. Chim. Phys.* [3], xlvi. 47.
[2] Scheurer-Kestner *Ibid.* [3], lvii. 23.
[3] Debray, *Compt. Rend* lxviii. 913.

Ferric Oxide and Lime, $Fe_2O_3.CaO$.[1] A crystalline compound having the above composition is obtained when an intimate mixture of 190 parts of sesquioxide of iron and 66·5 parts of lime is heated to whiteness in a platinum vessel for several hours. The product, which has been perfectly melted, is found on cooling to consist of a brittle mass of interlaced acicular crystals exceeding an inch in length, having a dark metallic lustre. Its specific gravity is 4·693; it yields a brown powder resembling brown iron ore, which is also obtained by precipitating a solution of ferric chloride, as nearly neutral as possible, with lime-water or saccharate of lime, and igniting the precipitate.

Ferric Oxide and Magnesia, $Fe_2O_3.MgO$, occurs in nature crystallising in black octohedrons as magnoferrite. It can be obtained artificially by the ignition of a mixture of the two oxides in a current of hydrochloric acid. The same compound is also formed when a mixture of ferric chloride and magnesium chloride is precipitated with a quantity of caustic soda insufficient to throw down the whole. On ignition a cinnabar-red powder of the above composition is obtained. Many analogous compounds can be prepared in a similar way.[2]

Ferric Oxide and Zinc Oxide, $Fe_2O_3.ZnO$. Obtained by Ebelmen, crystallised in black octohedrons, by strongly igniting both oxides together with boron trioxide. The mineral franklinite has a similar composition.

Certain of these magnetic compounds, such as those containing the oxides of copper and lead, are produced by the simple ignition of the oxides mixed in the proper proportions (List).

375 *Ferric Acid,* H_2FeO_4. This compound, like manganic acid, is not known in the free state. In the year 1702 Stahl noticed that when iron is fused with saltpetre and the solid mass lixiviated, or when a solution of iron in nitric acid is added to concentrated potash-ley, an amethyst or purple-red coloured solution is formed. Exactly a century afterwards Eckeberg published his Memoir on "Yttria," in which he states that when gadolinite is fused with potash and the fused mass extracted with water, the solution possesses a dark purple-red colour, due to iron and not to manganese. The potassium ferrate formed under these circumstances was more carefully examined by Fremy.[3] It is prepared by igniting iron-filings or iron oxide with saltpetre or

[1] Percy, *Phil. Mag.* [4], xlv. 455.
[2] List, *Ber. Deutsch. Chem. Ges.* xi. 1512.
[3] *Journ. Pharm.* xxvii. 97.

caustic potash, or a mixture of both. The formation of the compound may be readily shown by heating a mixture of one part of powdered iron with two parts of saltpetre in a small glass bulb, over a Bunsen burner. After a few minutes the mass becomes red-hot, and when cold the residue is dissolved in water. The purple solution is also obtained by passing chlorine through a strong solution of caustic potash, in which iron hydroxide is suspended (Fremy), and also by passing a current of electricity through a solution of caustic potash, the positive pole consisting of a plate of cast-iron, this solution after a time appearing almost black.[2] If more caustic potash be added to the concentrated and almost opaque solution a reddish-brown precipitate of potassium ferrate is formed. This may be dried on a porous plate, and then can be preserved in a sealed tube. It is a very unstable substance. Its solution becomes colourless on standing, and on heating ferrous hydroxide separates out with evolution of oxygen. Nitric acid and dilute sulphuric acid produce the same result, whilst hydrochloric acid decomposes it with evolution of chlorine.

Barium Ferrate, $BaFeO_4 + H_2O$, is obtained in the form of a dark red powder by precipitating the potassium salt with barium chloride. It is tolerably stable, and is soluble in acetic acid, yielding a red solution. When gently heated it becomes green, and when strongly heated it decomposes with evolution of oxygen and loss of water.

FERROUS SALTS.

376 The anhydrous ferrous salts of colourless acids are usually colourless, but the corresponding hydrated salts possess a light greenish-blue tint. The soluble salts possess a sweet, astringent ink-like taste. Their solutions readily absorb oxygen with formation of a ferric salt which is precipitated, when there is no excess of acid present, in the form of basic salt. In consequence of the ease with which they pass into a higher state of oxidation, the ferrous salts act as powerful reducing agents, and are largely employed for this purpose, both in the laboratory and in the workshop.

[1] Hofmann, *Ber. Deut. Chem. Ges.* ii. 239.
[2] Poggendorff, *Pogg. Ann.* liv. 373.

Ferrous Chloride, $FeCl_2$, is obtained by passing chlorine over iron filings (Thénard), but as a small quantity of ferric chloride is generally formed, even when an excess of iron is present, it is preferable to pass hydrochloric acid over iron filings, or iron wire heated to redness (Wöhler and Liebig), or to reduce ferric chloride by heating it in a stream of pure hydrogen. Ferrous chloride is deposited in colourless shining scales, which, according to Sénarmont, are six-sided. It has a specific gravity of 2·528 (Filhol), and is very deliquescent, dissolving readily in water and alcohol. It fuses at a red-heat, and volatilises at a temperature above the melting point of glass. When exposed to the air it oxidises to ferric chloride, which volatilises, and ferric oxide, which remains behind:

$$6FeCl_2 + O_3 = 2Fe_2Cl_6 + Fe_2O_3.$$

When heated in a current of steam magnetic oxide is formed:

$$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2.$$

When iron is dissolved in hydrochloric acid, and the solution concentrated in absence of air, bluish transparent monoclinic crystals of $FeCl_2 + 4H_2O$ are obtained; these have a specific gravity of 1·93, become greenish coloured on exposure to the air, effloresce at ordinary temperatures when kept over oil of vitriol, but deliquesce in the air. If a solution of this salt be evaporated with sal-ammoniac in absence of air, and the solid mass heated in a flask until the whole of the sal-ammoniac is volatilised, a residue of anhydrous ferrous chloride is left. Like other soluble ferrous salts, the solution of ferrous chloride absorbs nitric oxide, forming a dark greenish-brown solution, containing the compound $FeCl_2NO$. This substance is very unstable, losing the whole of its nitric oxide on warming, or when placed in a vacuum. The anhydrous chloride readily absorbs ammonia, swelling up to form a white powder (Faraday), having the composition $FeCl_2.6NH_3$ (Rostadius).

Ferrous Bromide, $FeBr_2$. When bromine vapour is passed over iron heated to dull redness, heat is evolved, and a yellowish crystalline deposit of ferrous bromide is formed (Liebig). An aqueous solution of ferrous bromide can easily be obtained by dissolving iron in hydrobromic acid, and on crystallising bluish-green rhombic tables are deposited, having the composition $FeBr_2 + 6H_2O$ (Löwig).

Ferrous Iodide, FeI_2, is obtained by triturating iodine with a slight excess of iron filings, or by heating iron filings in a covered porcelain crucible to redness, small quantities of iodine being gradually added; as soon as the whole mass becomes red-hot, a large quantity of iodine is thrown in, and the crucible heated until iodine vapour ceases to be given off. On allowing the crucible to cool it is found that a further evolution of iodine vapour takes place, a proof that the fused mass contains ferric iodide, which decomposes on cooling. The solid residue found is a grey lamino-crystalline mass, which melts at 177°.[1] If a mixture of iodine and iron filings be warmed with water, these elements combine with evolution of heat, and a colourless aqueous solution of ferrous iodide is obtained, which on exposure to the air readily oxidises with separation of iodine. This decomposition is prevented by the addition of sugar.

Ferrous Fluoride, FeF_2, is obtained in colourless or greenish prisms, $FeF_2 + 8H_2O$, by dissolving iron in hydrofluoric acid and evaporating; these crystals decompose when gently heated, leaving the anhydrous salt.

Ferrous Perchlorate, $Fe(ClO_4)_2 + 6H_2O$, is the only iron salt of the oxyacids of chlorine which is stable in the solid state. It is obtained by the double decomposition of ferrous sulphate and barium perchlorate (Serullas), or by dissolving iron in dilute perchloric acid (Roscoe). It forms very light green deliquescent crystals, which at 100 give off water, and decompose at a higher temperature.

Ferrous Sulphite, $FeSO_3$. When iron is dissolved in aqueous sulphurous acid in absence of air, no gas is evolved, and the solution contains ferrous sulphite and ferrous thiosulphite:

$$2Fe + 3H_2SO_3 = FeSO_3 + FeS_2O_3 + 3H_2O.$$

The latter salt is a very soluble one; the first, however, is only slightly soluble, so that after a short time it is deposited in colourless or greenish crystals. When freshly precipitated ferric hydroxide is dissolved in sulphurous acid, a red solution is obtained, which quickly becomes decolorised with formation of ferrous sulphite, and this contains an excess of sulphurous acid, whilst on the other hand, a solution of ferrous sulphite becomes red on exposure to the air.

377 *Ferrous Sulphate*, or *Green Vitriol*, $FeSO_4 + 7H_2O$, was

[1] Carius and Wanklyn, *Ann. Chem. Pharm.* cxx. 69.

probably used by Geber. Its preparation by dissolving iron in sulphuric acid was first described by Basil Valentine in his *Treatise on Natural and Supernatural Things:* "Take oleum vitrioli; dissolve therein *mars*, and prepare a vitriol from it." In his last volume he describes the method for preparing sulphide of iron and for obtaining from it vitriol: "*Limaturam ferri* and *sulphur ana* calcined in a potter's furnace until it becomes tinted purple; then pour upon this distilled water, when a fine green liquid is formed. Draw this off *ad tertias*, allow it to deposit, and thus obtain an artificial vitriol." Agricola in his discourse *De re Metallica* mentions two kinds of pyrites. The one, such as coal-brasses, decomposes spontaneously and yields a vitriol; whilst the other, as the ordinary Mason's pyrites, does so only when it is roasted. Green vitriol occurs as the mineral melanterite, either crystalline or in fibrous stalactitic forms, but generally massive and pulverulent. It is usually derived from the decomposition of pyrites or marcasite. Ferrous sulphate is likewise frequently found in solution in drainage water from mines, and it is manufactured on a large scale from this source. Large quantities of green vitriol (about 100 tons per week) are manufactured in South Lancashire from the pyrites occurring in the coal-measures. These are piled up in heaps and exposed to the atmosphere. The soluble ferrous sulphate together with the excess of sulphuric acid formed, runs into underground tanks, where the excess of acid is removed by means of scrap-iron. On evaporating the liquor large crystals of ferrous sulphate are obtained. Iron sulphate is also formed as a bye-product in the manufacture of copper sulphate or blue vitriol (see par. 193). The commercial salt not unfrequently contains traces of copper sulphate, and this may be detected and separated, as was pointed out so long ago as 1683 by Vigani, by leaving the solution in contact with metallic iron until the whole of the copper is precipitated. Another common impurity is ferric sulphate; this may be removed by recrystallisation, but zinc sulphate, manganese sulphate, and other salts cannot thus be got rid of. Hence when chemically pure ferrous sulphate is needed, it is best to dissolve iron wire in dilute sulphuric acid. When the evolution of hydrogen has ceased, the liquid is boiled together with the undissolved portion of the wire, filtered and evaporated to crystallisation.

Ferrous sulphate forms well-defined monoclinic crystals (Fig. 156), having a specific gravity of 1·889° at 4° (Joule and Playfair).

One hundred parts of water dissolve, according to Brandes and Firnhaber, the following:—

At	10°	15°	33°	60°	90°	100°
$FeSO_4 + 7H_2O$ . .	61	70	151	263	370	333

Ferrous sulphate is dimorphous, often crystallizing in rhombic prisms, which are isomorphous with zinc sulphate. These are easily obtained when a crystal of zinc sulphate is thrown into a supersaturated solution of the ferrous salt. But, on the other hand, if a crystal of copper sulphate be employed, triclinic

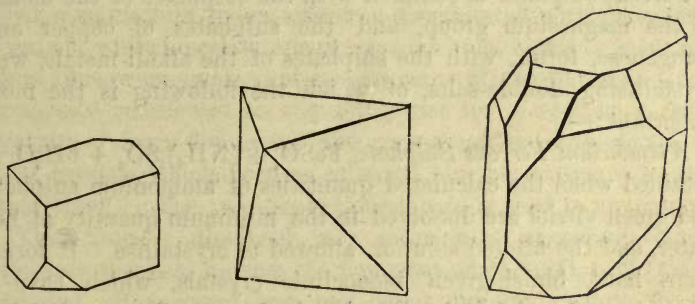


Fig. 156.

crystals having the composition $FeSO_4 + 5H_2O$ are obtained (Lecoq de Boisbaudran). These last are also deposited when a solution of ferrous sulphate containing free sulphuric acid is allowed to evaporate in a vacuum. Crystals of green vitriol first separate, and then the penta-hydrated salt, whilst at last crystals of a tetra-hydrate, $FeSO_4 + 4H_2O$, are deposited, and these are isomorphous with the corresponding manganese sulphate. When iron sulphate is heated in a vacuum to 140°, it yields a white powder of the monohydrate $FeSO_4 + H_2O$, and this, when gently heated in absence of air, yields the anhydrous salt, $FeSO_4$.

Ferrous sulphate is insoluble in concentrated sulphuric acid and absolute alcohol, whilst it dissolves slightly in dilute alcohol. Hence sulphuric acid and alcohol precipitate the solution of the sulphate, the precipitate containing varying quantities of water of crystallisation according to the quantity of the precipitant and the concentration of the solution. A solution of ferrous sulphate, like the chloride, absorbs nitric oxide. The dark brown saturated solution, which probably contains the compound

$FeSO_4.NO$, gives off the gas in a vacuum as well as when heated; in the latter case small quantities of nitrogen monoxide and ferric sulphate are formed. When the brown solution is mixed with strong sulphuric acid, care being taken to keep the mixture cool, it becomes of a purple-red colour; and upon this reaction the well-known test for nitric acid and the nitrates depends, as well as the method of detecting the presence of nitrous fumes in sulphuric acid.

Green vitriol is largely used in the arts and manufactures for the preparation of iron-mordants, inks, Prussian blue, &c.

Ferrous sulphate is common with the sulphates of the metals of the magnesium group, and the sulphates of copper and manganese, forms, with the sulphates of the alkali-metals, well crystallising double-salts, of which the following is the most important:—

Ammonium Ferrous Sulphate, $FeSO_4 + (NH_4)_2SO_4 + 6H_2O$, is obtained when the calculated quantities of ammonium sulphate and green vitriol are dissolved in the minimum quantity of hot water, and the filtered solution allowed to crystallise. It forms clear, hard, bluish-green monoclinic crystals, which have a specific gravity of 1·813. One hundred parts of water dissolve (Tobler):—

At	0°	20°	30°	60°	75°
$FeSO_4 + (NH_4)_2SO_4$.	12·2	21·6	28·1	44·6	56·7

This salt is a very stable one, and does not undergo alteration in the air, being much less easily oxidised than green vitriol itself. Hence it is largely used instead of the latter salt for the purposes of volumetric analysis, in chlorimetry, &c. This salt when in large crystals, frequently contains included mother-liquor, and hence when the pure salt is needed it is best to add alcohol to the concentrated solution, when a crystalline precipitate of the salt is formed, and this is afterwards dried.

Ferrous Disulphate, FeS_2O_7, separates out as a white powder when a concentrated solution of iron sulphate is mixed with several times its volume of concentrated sulphuric acid. It forms microscopic prisms, and is decomposed by water into sulphuric acid and green vitriol.[1]

378 *Ferrous Nitrate*, $Fe(NO_3)_2$, is best obtained by the decomposition of green vitriol with barium nitrate, the filtrate being evaporated in a vacuum over sulphuric acid. It is very soluble

[1] Bolas, *Journ. Chem. Soc.* for 1874, 212.

in water and very unstable, easily passing into ferric nitrate. When iron is dissolved in cold dilute nitric acid, the following reaction takes place (Berzelius):

$$8Fe + 20HNO_3 = 8Fe(NO_3)_2 + 2NH_4NO_3 + 6H_2O.$$

Ferrous Phosphate, $Fe_3(PO_4)_2 + 8H_2O$, occurs as the mineral vivianite, crystallising in monoclinic prisms. In its pure state it is colourless, but it generally possesses a green or blue tint, owing to partial oxidation. It is also found as an earthy mass termed blue iron-earth, sometimes dispersed through clay, and together with bog-iron ore, and in the cavities in fossil bones. When a solution of green vitriol is precipitated with phosphate of soda, a white precipitate is obtained, which, however, soon becomes blue or green on exposure to air. If the liquid and the precipitate be allowed to stand together for a week at a temperature of from 60° to 80° the compound is converted into small crystals which become coloured blue on exposure to the air (Debray). The precipitated phosphate is used in medicine.

When iron is dissolved in a solution of phosphoric acid, colourless needles, having the composition $HFePO_4 + H_2O$, are deposited after some time, and these become slightly blue-coloured on exposure to air.

Ferrous Carbonate, $FeCO_3$, occurs naturally as spathose iron-ore, which, however, contains larger or smaller quantities of the carbonates of calcium, manganese, and magnesium. The mineral is obtained artificially in microscopic rhombohedrons by precipitating a solution of green vitriol with bicarbonate of soda and heating the mixture for from twelve to thirty-six hours to a temperature of 150° (Sénarmont). When a cold solution of pure ferrous sulphate is precipitated with sodium carbonate, a flocculent white precipitate is thrown down which rapidly becomes of a dirty green colour from absorption of oxygen from the air and evolution of carbon dioxide, at last being wholly converted into ferric hydroxide. If the precipitate be washed in total absence of air, it may be obtained pure and colourless. Usually, however, it takes the form of a greyish powder, which is soon oxidised on exposure to the air. If the moist precipitate be mixed with sugar it does not undergo such rapid change.

FERRIC SALTS.

379 In the anhydrous state the ferric salts are generally colourless. In the hydrated state they are yellow or brown. The soluble ferric salts possess a peculiar astringent taste, and they pass readily by reduction into the corresponding ferrous compounds.

Ferric Chloride, Fe_2Cl_6. The aqueous solution of this salt was known to Glauber under the name of *oleum martis*. He obtained it in the dry state by dissolving iron in hydrochloric acid and evaporating the solution in a flask: "*In fundo* there remains a blood red *massa*, which is as hot to the tongue as fire. It must be well kept from the air, otherwise it liquefies to a yellow *oleum*."

Anhydrous ferric chloride is obtained by heating iron wire in a current of dry chlorine gas at a moderate red-heat, when rapid combination with ignition takes place, ferric chloride being deposited. It is also produced when hydrochloric acid is passed over heated amorphous ferric oxide, and it is not unfrequently found in the craters of volcanoes.

Ferric chloride forms iron-black iridescent plates or sometimes large hexagonal tables, which exhibit a red colour by transmitted and a green metallic lustre by reflected light. It is very deliquescent and easily soluble in water, alcohol, and ether. When heated strongly it volatilises, giving rise to a vapour having a specific gravity of 11·39.[1]

Ferric chloride forms with ammonia the compound $Fe_2Cl_6 + 2NH_3$, which does not differ in appearance from ferric chloride itself. It slowly deliquesces on exposure to the air, forming a clear dark-red liquid. Ferric chloride also combines with phosphorus pentachloride, the compound $Fe_2Cl_6 + 2PCl_5$ being formed as a brown, easily fusible mass. It also absorbs nitrosyl chloride yielding a dark-coloured deliquescent compound $Fe_2Cl_6 + 2NOCl$. When heated in a current of steam it is decomposed into ferric oxide and hydrochloric acid, and when heated in oxygen, chlorine is evolved, ferric oxide remaining.

For the purpose of obtaining a solution of ferric chloride, the hydroxide may be dissolved in hydrochloric acid and the liquid evaporated in order to drive off excess of acid. Or a solution of ferrous chloride may be heated with the requisite quantity of

[1] Deville and Troost, *Compt. Rend.* xlv. 821.

hydrochloric acid and the heated solution oxidised by addition of nitric acid. The solution of ferric chloride is, however, best prepared by dissolving iron wire in hydrochloric acid, as described under the preparation of ferrous chloride, and then passing chlorine into this solution until, after standing for some time, it smells strongly of the gas. The excess of chlorine is then displaced by passing a current of carbon dioxide through the warm liquid. A concentrated solution of ferric chloride has a dark brown colour and an oily consistency. On dilution it becomes limpid, and has a slightly yellow colour. Its specific gravity at 17° is as follows (Fremy):—

Percentage of Fe_2Cl_6.	Specific Gravity.	Percentage of Fe_2Cl_6.	Specific Gravity.
1	1·0073	40	1·3622
10	1·0734	50	1·4867
20	1·1542	60	1·6317
30	1·2658		

When 100 parts of ferric chloride are dissolved in 63·5 parts of water a liquid is obtained which has a specific gravity of 1·67 at 25°, and this solidifies to a yellow crystalline mass, having the composition $Fe_2Cl_6 + 12H_2O$. The same compound is formed when the deliquescent anhydrous chloride is exposed to moist air. When the crystals are fused and the liquid concentrated to a syrupy consistency, and a few drops of hydrochloric acid added, yellow rhombic tables having the composition $Fe_2Cl_6 + 6H_2O$ are deposited, and these are very hygroscopic. The aqueous solution of the normal chloride is decomposed on heating, and the more easily the more dilute the solution is, an insoluble oxychloride or soluble ferric hydroxide being produced according to the concentration of the liquid.

The solutions of ferrous and ferric chlorides have long been used in medicine. An alcoholic solution of ferric chloride was formerly employed as a quack medicine of repute, known by the name of Lamotte's golden drops. This solution loses its colour when exposed to light, ferrous chloride being formed, the latter compound separating, when the solution is not too dilute, in fine green crystals, $FeCl_2 + 2H_2O$.

Ferroso-ferric Chloride, $Fe_3Cl_8 + 18H_2O$. Magnetic oxide of iron dissolves readily in concentrated hydrochloric acid, forming a yellow liquid, which on concentration over sulphuric acid

deposits the above salt in opaque yellow deliquescent crystalline crusts.

Ferric chloride forms garnet-red-coloured crystalline double salts with the chlorides of the alkali metals, such as $Fe_2Cl_6 + 4KCl + 2H_2O$ and $Fe_2Cl_6 + 4NH_4Cl + 2H_2O$. These are decomposed by water, and a mixture of the latter salt with an excess of sal-ammoniac is termed iron-sal-ammoniac; it was formerly obtained by sublimation of a mixture of iron oxide and ammonium chloride, and is mentioned by Basil Valentine. Sal-ammoniac crystallises in yellow or bright red transparent regular crystals from a dilute solution of ferric chloride; these contain a varying amount of iron and rapidly absorb moisture from the air.

380 *Iron Oxychlorides.* These compounds are formed in various ways. Some are soluble, whilst others are insoluble in water. When freshly precipitated ferric hydroxide is added to a solution of ferric chloride, it dissolves in considerable quantity, and a dark-red liquid is obtained which to one molecule of chloride may contain twenty or more molecules of oxide, and this on dialysis furnishes Graham's soluble oxide. These solutions may be diluted or warmed without any precipitation of ferric oxide. Many acids and salts, however, precipitate either ferric hydroxide or a basic chloride from these solutions, which latter is again soluble in water. If ferric chloride be incompletely precipitated with alkalis, a precipitate is also obtained which is soluble in water when it does not contain more oxide than is indicated by the formula, $Fe_2Cl_6 + 5Fe_2(OH)_6 = Fe_2(OH)_5Cl$.

Insoluble basic ferric chlorides are formed, in the first place, by the oxidation of ferrous chloride in the air; secondly, by roasting iron in the presence of hydrochloric acid or a chloride; and, thirdly, by boiling a solution of ferric chloride for some time. The composition and colour of these salts vary according to the mode of preparation. They are generally difficultly soluble in hydrochloric acid.

Ferric Bromide, Fe_2Br_6. This is obtained in the form of dark-red crystals by heating iron in an excess of bromine vapour. When heated in absence of air it fuses, and a part may be sublimed without decomposition, another portion, however, being decomposed into ferrous bromide and free bromine. The bromide deliquesces on exposure to air, and the solution, which may be simply obtained by dissolving the hydroxide in hydrobromic acid, decomposes on evaporation, with formation of insoluble

basic bromides. Like the chloride, the solution of the bromide dissolves ferric hydroxide readily with formation of soluble oxybromides.

Ferric Fluoride, Fe_2F_6, is obtained by dissolving the hydroxide in hydrofluoric acid, colourless crystals of $Fe_2F_6 + 9H_2O$ separating out on evaporation. These lose their water when heated, and may be fused in a platinum crucible over the blowpipe, when crystals sometimes form on the surface which are isomorphous with aluminium fluoride. The anhydrous salt dissolves slowly but completely in water.

381 *Ferric Sulphate*, $Fe_2(SO_4)_3$, is obtained by the action of nitric acid on a hot solution of green vitriol, to which the requisite quantity of sulphuric acid has been added:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

The yellowish-brown solution gives a syrupy liquid when concentrated, from which colourless crystals are deposited on standing. When these are heated, or when sulphuric acid is added to the concentrated solution, the anhydrous salt is formed as a white powder, whilst by the action of green vitriol on boiling sulphuric acid the same salt is deposited in small crystalline scales or rhombic prisms:

$$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 2H_2O.$$

The anhydrous salt dissolves slowly in water and it is decomposed on heating into ferric oxide and sulphur trioxide. When a dilute solution of ferric sulphate is boiled or incompletely precipitated with alkalis, or when a solution of green vitriol is allowed to oxidise in the air, various basic ferric sulphates are formed. An iron mordant obtained by oxidising green vitriol with nitric acid deposits on standing large transparent crystals, which are probably monoclinic, having the composition $Fe_2(SO_4)_2(OH)_2 + 14H_2O$; these are decomposed by water with formation of the insoluble salt $Fe_2SO_4(OH)_4 + 5H_2O$.[1] Various other basic ferric sulphates occur as minerals, being formed by the oxidation of the sulphides of iron. Amongst these may be mentioned vitriol ochre, $FeSO_4(OH)_4 + Fe_2(OH)_6 + H_2O$. This frequently occurs in long brown, green, or ochrey yellow stalactites; whilst copiapite, $Fe_2(SO_4)_3 + Fe_2(SO_4)_2(OH)_2 + 10H_2O$, occurs in sulphur yellow tables or crystalline scales, and fibro-

[1] *Ber. Deutsch Chem. Ges.* viii. 77.

ferrite, $2Fe_2(SO_4)_2(OH)_2 + Fe_2SO_4(OH)_4 + 24H_2O$, forms a pale-yellow or nearly white pearly or silky mass.

Ferroso-ferric Sulphates. The two sulphates of iron form various double salts, of which some are found in the mineral kingdom. Amongst these is roemerite, $Fe_3(SO_4)_4 + 12H_2O$, forming yellow monoclinic crystals, occurring at the Rammelsberg mine, near Goslar, together with another similar mineral termed voltaite, in which a part of the iron is replaced by isomorphous metals.

Ferric Potassium Sulphate or *Iron Alum*, $Fe_2(SO_4)_3 + K_2SO_4 + 24H_2O$, is obtained when the proper quantity of potassium sulphate is added to a solution of ferric sulphate and the concentrated solution allowed to stand for some days about 0°. The salt forms bright violet octohedrons and dissolves in about five parts of cold water. If caustic potash is added to the solution and the dark liquid allowed to evaporate, transparent yellowish-brown hexagonal crystals separate out which have the composition $5K_2SO_4 + 2Fe_2(SO_4)_2(OH)_2 + 16H_2O$, and possess the peculiar optical properties of tourmaline. This salt easily decomposes into iron-alum and an insoluble basic ferric salt.

382 *Ferric Nitrate*, $Fe_2(NO_3)_6$, is formed by dissolving iron in nitric acid. The brown concentrated solution deposits, on addition of nitric acid, according to the quantity of the same or the concentration of the solution, colourless cubes of $Fe_2(NO_3)_6 + 12H_2O$, or colourless monoclinic crystals containing 18 molecules of water. These are very deliquescent, and dissolve in water forming a brown liquid. Ferric nitrate is used as a mordant in dyeing and calico-printing.

Several soluble and several insoluble basic ferric nitrates are known.

Ferric Phosphates. The normal orthophosphate, $Fe_2(PO_4)_2 + 4H_2O$, is obtained as a yellowish-white precipitate by adding phosphate of soda to normal ferric chloride. This is soluble in dilute mineral acids, but not in cold acetic acid. On strongly heating it loses its water and becomes yellow.

When ferric sulphate is precipitated with an excess of ammonium phosphate, a crystalline precipitate of $2Fe_2(PO_4H)_3 + 5H_2O$ is thrown down. Basic iron phosphates occur in nature, and frequently form a constituent of limonite. It also occurs as dufrenite, $Fe_2(OH)_3PO_4$, which is found sometimes in rhombic crystals, but more generally in needles or as a radiated fibrous mass. Vivianite (see p. 97) is often oxidised and is converted

into beraunite, $Fe_2(PO_4)_2 + 4Fe_2PO_4(OH)_3 + 8H_2O$, occurring in small foliated aggregations having a hyacinth-red colour.

Ferric Arsenite. The basic salt, $Fe_4O_5(OH)_5As = 4Fe_2O_3 + As_2O_3 + 5H_2O$, is a voluminous brown precipitate closely resembling ferric hydroxide in appearance. It is obtained by adding an aqueous solution of arsenic trioxide, or an arsenite, to ferric acetate. This compound is also formed when a solution of arsenic trioxide is shaken with freshly precipitated ferric oxide, and for this reason this latter compound is used as an antidote in case of arsenical poisoning. (See Vol. I. p. 528.)

Ferric Arsenates. The normal arsenate occurs as scorodite, $Fe_2(AsO_4)_2 + 4H_2O$, in brown rhombic vitreous crystals. Basic arsenates are also found in the mineral kingdom; amongst these we have iron-sinster or pharmacosiderite, $Fe_2(AsP)_2O_8 + Fe_2(AsP)O_4(OH)_3 + 6H_2O$, which occurs crystallised in the regular system in green or brownish-green adamantine crystals. The acid arsenate, $2Fe_2(HAsO_4)_3 + 9H_2O$, is a white precipitate obtained by adding hydrogen disodium arsenate to a solution of ferric chloride. It is easily soluble in hydrochloric acid, and separates on evaporation as a white powder.

Silicates of Iron. Several ferrous and ferric silicates occur in the mineral kingdom, but they are more frequently found as double silicates, in which the alkali metals and the metals of the alkaline earths are present. These are generally isomorphous mixtures in which ferric oxide is replaced by alumina, whilst lime, magnesia, and the alkalis are substituted by ferrous oxide, manganous oxide, &c. For a description of these compounds works on mineralogy must be consulted.

The Iron Tree. In Glauber's description of the preparation of *oleum martis* (see p. 98) the following passage occurs:—"When such a red *massa* before it deliquesces to an *oleum* is laid in *oleum arenæ vel silicum* for one or two hours, a tree grows out of it, with roots, stems, many branches, and twigs, wonderful to behold." This phenomenon depends upon the fact that water-glass, which always contains some carbonate, decomposes the ferric chloride into ferric silicate and basic ferric carbonate, whilst bubbles of carbon dioxide are given off, and thus filiform processes are produced. In place of the ferric chloride, ferrous chloride, cobalt chloride, nickel chloride, copper nitrate, and many other easily soluble metallic salts may be employed, and thus a series of coloured coral-like growths may be produced.

IRON AND CYANOGEN.

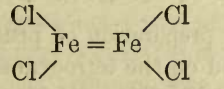
383 Our knowledge of the peculiar compounds of iron and cyanogen commences with the discovery of Prussian blue, which, as has been stated (Vol. I. p. 655), was made early in the 18th century by a colour-maker named Diesbach. In 1752 Macquer observed that when this colour is boiled with caustic potash oxide of iron remains, whilst a peculiar salt enters into solution which was named phlogisticated alkali or yellow prussiate of potash. This body was shown to contain iron and prussic acid by Berthollet in 1787. Proust, in 1806, next found that iron remains in combination with prussic acid when the alkali in the yellow prussiate is replaced by other bases; and Ittner in 1809 considered that the compounds of ferric oxide and other bases with prussic acid are double salts. In opposition to this view R. Porret[1] in 1814-15 published a series of experiments founded on a suggestion of Berthollet's, from which he drew the conclusion that the so-called double prussiates containing iron are simple salts of a compound acid containing ferrous oxide and prussic acid, to which he gave the name of *ferruretted chyazic acid*, a name derived from the fact that it is a compound of carbon, hydrogen, and azote or nitrogen. Gay-Lussac's classical investigation of prussic acid followed immediately on Porret's memoir. In this he proved that the acid is a hydrogen compound of the radical cyanogen. Berzelius then showed that all the salts of iron and prussic acid may be considered to be double cyanides, and that (according to our present nomenclature) the prussiate of potash is a cyanide of iron and potassium, $Fe(CN)_2 + 4KCN$. Three years later Gmelin[2] obtained a new compound by acting upon this salt with chlorine, which from its red colour was termed red prussiate of potash. This may be regarded as the ferric double salt, $Fe_2(CN)_6 + 6KCN$. Gmelin likewise proved that the potassium in the salt may be replaced by hydrogen, thus giving rise to ferricyanic acid. In the following year Gay-Lussac pointed out that the yellow prussiate may be supposed to contain a compound radical consisting of iron and cyanogen, to which he gave the name *cyanoferre*. Liebig extended this explanation to the other cyanogen compounds containing iron, and considered the above salt as compounds of two isomeric

[1] *Phil. Trans.* 1814. 527; *Ann Phil.* xii. 214, and xiv. 295.
[2] *Schweigg. Journ.* xxxiv. 325.

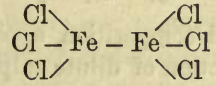
radicals, C_6N_6Fe, to which he gave the names of *ferrocyanogen* and *ferricyanogen*, indicating their composition by the symbols Cfy and Cfdy.[1]

Graham assumed that these compounds contained the radical of cyanuric acid, tricyanogen, C_3N_3, to which he gave the name of *prussine*, and according to this view the composition of these compounds can be easily explained.[2] If we consider iron as a tetrad element, the following simple formulæ represent the constitution of its chlorides:

Ferrous Chloride.

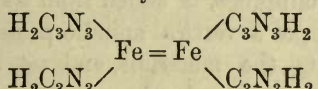


Ferric Chloride.

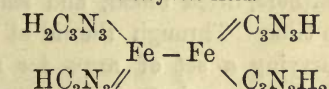


If we now suppose that each atom of chlorine is replaced by the triad group tricyanogen, the octad radical ferrocyanogen is obtained; and, in a similar way, the hexad ferricyanogen is formed by the replacement of the six atoms of chlorine by four tricyanogen groups. The acids which are thus formed have then the following constitution:[3]

Ferrocyanic Acid.



Ferricyanic Acid.



FERROCYANOGEN COMPOUNDS.

384 *Hydrogen Ferrocyanide or Ferrocyanic Acid*, $H_8(C_3N_3)_4Fe_2$. This is best obtained when pure hydrochloric acid is added to an equal volume of a cold saturated solution of potassium ferrocyanide. The precipitate which forms is dried on a porous plate in absence of air, then dissolved in alcohol, and precipitated by ether.[4] It is a white powder crystallising in small needles. Larger crystals may be obtained by pouring a layer of ether on to the alcoholic solution. Ferrocyanic acid is easily soluble in water and alcohol. It possesses a strongly acid taste and reaction, and is so powerful an acid that it liberates not only acetic, but even oxalic acid from its salts. It oxidises

[1] *Handwörterbuch*, iii. 66.
[2] *Elements of Chemistry*, i. 200.
[3] Erlenmeyer, *Lehrbuch Org. Chem.*
[4] Liebig, *Ann. Pharm.* lxxxvii. 127.

quickly on exposure to air, especially when warmed with formation of hydrocyanic acid and Williamson's blue.

$$7H_8(CN)_{12}Fe_2 + 2O_2 = 48HCN + 2Fe_7(CN)_{18} + 4H_2O.$$

This reaction is employed in calico-printing, the cloth being printed with a mixture of tartaric acid and yellow prussiate, and then steamed. When the solution of the acid is boiled, hydrocyanic acid is evolved and a white precipitate of acid ferrous ferrocyanide remains behind:[1]

$$2H_8(CN)_{12}\overset{iv}{Fe}_2 = 12HCN + H_4\overset{iv}{Fe}_2(C_{12}N_{12}\overset{iv}{Fe}_2).$$

This decomposition explains the preparation of prussic acid by the action of dilute sulphuric acid on the ferrocyanide.

385 *Potassium Ferrocyanide*, $K_8(C_3N_3)_4Fe_2 + 6H_2O$ or $K_4Cfy + 3H_2O$. This salt, generally known under the old name of yellow prussiate of potash, serves as the point of departure for the preparation of almost all the cyanogen compounds. It is obtained by heating crude potashes in cast-iron, hemispherical pots set in brickwork and heated by a fire with a circular flue. Each pot is closed by an iron lid having an aperture through which a mixture of iron filings and animal matter, such as horn, feathers, dried blood, and leather-clippings, is added from time to time. Through the lid of each pot a vertical spindle passes, carrying a set of arms for mixing the materials, and set in motion by a shaft driven by steam-power. In this operation a portion of the nitrogen is evolved as ammonia and forms potassium cyanide at the same time that the sulphur contained in the animal matter, as well as that contained as potassium sulphate in the potashes, gives rise to potassium iron sulphide, $K_2S + Fe_2S_3$, a compound which will be described afterwards. When the resulting fused mass, or "metal" as it is termed, is lixiviated, yellow prussiate of potash is formed according to the following equation:[2]

$$13KCN + Fe_2S_3 = K_8(CN)_{12}Fe_2 + 2K_2S + KSCN.$$

In this operation the iron pots are very quickly attacked by the sulphur contained in the materials, and a further loss occurs owing to the formation of potassium thiocyanate. A better yield is obtained when potash free from sulphate is used, and on lixiviating the mass freshly precipitated ferrous carbonate,

[1] Riemann and Carius, *Ann. Chem. Pharm.* cxiii. 39.
[2] Preis, *Journ. Pract. Chem.* cvii. 10.

obtained by dissolving chalk or limestone in a solution of ferrous chloride, is added, this acting on the potassium cyanide as follows:

$$12KCN + 2Fe_2CO_3 = K_8(CN)_{12}Fe_2 + 2K_2CO_3.$$

The solution is evaporated to a specific gravity of 1·27, and then run into crystallising vessels, where it deposits the crude salt. This is again dissolved in warm water to form a solution having the same strength as before, and again crystallised, the mother-liquors being drawn off and used to dissolve fresh quantities of the crude salt. It has already been stated that in the preparation a part of the nitrogen is lost as ammonia, and a further loss occurs through the formation of thiocyanate and cyanate. In consequence of this, many attempts have been made to improve the yield, but, up to the present time, without success. For various reasons the manufacture of prussiate of potash has lately lost much of its importance.

Potassium ferrocyanide is also formed when a ferrous salt is mixed with an excess of potassium cyanide. In this case a brown precipitate is first formed, which was supposed to be ferrous cyanide, but is now known to contain potassium cyanide, and probably has the formula $Fe_2(CN)_5K$. This readily dissolves in potassium cyanide:

$$Fe_2(CN)_5K + 7KCN = Fe_2(CN)_{12}K_8.$$

A solution of potassium cyanide in absence of air dissolves metallic iron with evolution of hydrogen slowly in the cold and more quickly when heated:

$$12KCN + 2Fe + 4H_2O = Fe_2(CN)_{12}K_8 + 4KOH + 2H_2.$$

Potassium ferrocyanide forms quadratic pyramids in which the basal faces are usually dominant, Fig. 157. They are of a lemon yellow colour, and generally opaque. Small crystals on the other hand, are amber-coloured and transparent. The specific gravity is 1·83. It does not undergo alteration in pure air at the ordinary temperature, but when heated to 60° it begins to lose its water of crystallisation, which is completely given off at 100°, the anhydrous salt remaining as a white powder. It has a sweetish saline and somewhat bitter taste, and is not poisonous, acting in large doses as an aperient. Four parts

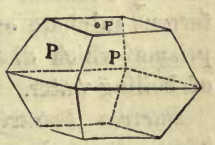


FIG. 157.

of cold, and two parts of boiling water dissolve the salt, which is insoluble in alcohol, and is precipitated from aqueous solution by this liquid in yellowish-white pearly scales. When its solution is exposed to light for some time Prussian blue separates out, and on boiling the solution in the air ammonia is given off and the liquid becomes alkaline. The commercial salt frequently contains considerable quantities of potassium sulphate which can be removed by recrystallisation only with difficulty.

Sodium Ferrocyanide, $Na_8(C_3N_3)_4Fe_2 + 24H_2O$, is best obtained by boiling Prussian blue with caustic soda, when yellow, transparent monoclinic prisms are found which effloresce in warm air.

Sodium Potassium Ferrocyanide, $Na_2K_6(C_3N_3)_4Fe_2 + 7H_2O$, is obtained when the corresponding ammonium salt is boiled with caustic soda. It crystallises in four-sided prisms which are easily soluble in water.

Ammonium Ferrocyanide, $(NH_4)_8(C_3N_3)_4Fe_2 + 6H_2O$, is prepared by saturating ferrocyanic acid with ammonia or by digesting the lead salt with ammonium carbonate. It crystallises in yellow prisms, and is isomorphous with the potassium salt.

Ammonium Potassium Ferrocyanide, $(NH_4)_2K_6(C_3N_3)_4Fe_2$, is formed when an ammoniacal solution of potassium ferricyanide is treated with reducing agents, such as grape-sugar. It crystallises in quadratic prisms, and is easily soluble in water.

Calcium Ferrocyanide, $Ca_4(C_3N_3)_4Fe_2 + 24H_2O$, is formed when Prussian blue is boiled with the exactly requisite quantity of milk of lime, or when calcium carbonate is dissolved in hydroferrocyanic acid. It is very soluble in water, depositing in flat yellow triclinic prisms which have an unpleasant bitter taste.

Strontium Ferrocyanide, $Sr_4(C_3N_3)_4Fe_2 + 30H_2O$, is prepared in a similar way to the calcium salt, and forms fine monoclinic readily soluble crystals.

Barium Ferrocyanide, $Ba_4(C_3N_3)_4Fe_2 + 6H_2O$, is obtained by boiling Prussian blue with baryta water, or by the action of ferrous sulphate on barium cyanide. It forms flat monoclinic prisms which dissolve in 584 parts of cold, and 116 parts of boiling water.

Barium Potassium Ferrocyanide, $K_4Ba_2(C_3N_3)_4Fe_2 + 6H_2O$. This salt is deposited in small yellow rhombohedrons when boiling saturated solutions of 2 parts of ferrocyanide of potassium and 1 part of barium chloride are mixed, and the mixture allowed to cool. It dissolves in 38 parts of cold, and

9·5 parts of boiling water. This salt is much employed for the preparation of the other double ferrocyanides of potassium which may all be obtained by the action of the corresponding sulphates upon the salt. When a hot solution of ferrocyanide of potassium is treated with an excess of barium chloride, a mixture of the double salt with barium ferrocyanide is obtained, and the whole is converted into the latter salt when the precipitate is boiled with a solution of barium chloride.

Zinc Ferrocyanide, $Zn_4(C_3N_3)_4Fe_2$, is a white precipitate used in medicine.

Copper Ferrocyanide, $Cu_4(C_3N_3)_4Fe_2$, is a fine brown precipitate known as Hatchett's brown.

The ferrocyanides of most of the other metals are either difficultly soluble or insoluble in water. Some of them possess characteristic colours, especially those of copper and uranium, &c., and for this reason potassium ferrocyanide is used as a test for these metals.

FERRICYANOGEN COMPOUNDS.

386 *Ferricyanic Acid*, $H_6(C_3N_3)_4Fe_2 = 2H_3Cfdy$. This is obtained by decomposing the lead salt with dilute sulphuric acid, and evaporating the solution at a moderate temperature. The acid crystallises in brown needles and has an astringent acid taste.

Potassium Ferricyanide, $K_6(C_3N_3)_4Fe_2$, is generally known under the name of red prussiate of potash, and is formed when potassium ferrocyanide is treated with oxidising agents. It is obtained on the large scale by passing chlorine into a solution of the yellow prussiate:

$$K_8(C_3N_3)_4Fe_2 + Cl_2 = K_6(C_3N_3)_4Fe_2 + 2KCl.$$

It may be readily separated from the potassium chloride formed at the same time by repeated crystallisation. It forms large dark red monoclinic prisms (Figs. 158 and 159), which have a specific gravity of 1·8, and frequently occurs in twin form exhibited by Fig. 159. It possesses a faintly astringent and saline taste, and yields a dark yellow powder. It dissolves in water giving a yellowish-brown solution, which on dilution assumes a lemon-yellow colour. One hundred parts of water dissolve:[1]

[1] Wallace, *Journ. Chem. Soc.* vii. 80.

At	4°·4	10°	15°·6	37°·8	100°
$K_6(C_3N_3)_4Fe_2$	33·0	36·6	39·7	58·8	77·6

and 82 parts at 104°, the boiling-point of the saturated solution. It is only slightly soluble in alcohol. When exposed to light the solution becomes darker, and a blue precipitate is formed, ferrocyanide remaining in solution. When the salt is heated in a flame it burns, and when mixed with nitrate of ammonia and

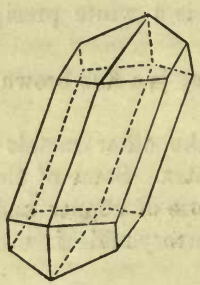


FIG. 158.

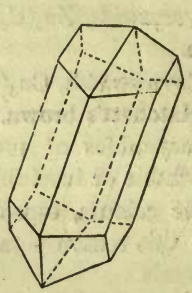


FIG. 159.

heated the mixture detonates. It is a powerful oxidising agent, especially in alkaline solution, converting the monoxides of lead and manganese into dioxides, and forming potassium chromate and ferrocyanide of potassium, when boiled with solution of chromium sesquioxide in potash:

$$3K_6(C_3N_3)_4Fe_2 + Cr_2O_3 + 10KOH = 3K_8(C_3N_3)_4Fe_2 + 2K_2CrO_4 + 5H_2O.$$

When its solution is acted upon by sodium amalgam, sodium potassium ferrocyanide is formed. Hydrogen dioxide converts potassium ferricyanide into ferrocyanide:

$$4K_6(C_3N_3)_4Fe_2 + 4H_2O_2 = 3K_8(C_3N_3)_4Fe_2 + H_8(C_3N_3)_4Fe_2 + 4O_2,$$

whilst on the other hand hydrogen dioxide oxidises a neutral solution of the yellow salt to ferricyanide (Weltzien):

$$K_8(C_3N_3)_4Fe_2 + H_2O_2 = K_6(C_3N_3)_4Fe_2 + 2KOH.$$

Sodium Ferricyanide, $Na_6(C_3N_3)_4Fe_2 + H_2O$, is obtained by the action of chlorine upon sodium ferrocyanide. It dissolves in 1·25 parts of boiling, and 5·3 parts of cold water, and crystallises in ruby-red four-sided prisms which deliquesce on exposure to air.

Potassium Sodium Ferricyanide, $Na_3K_3(C_3N_3)_4Fe_2$, crystallises

in fine red cubes which are formed when the sodium and potassium salts are allowed to crystallise together.

Ammonium Ferricyanide, $(NH_4)_6(C_3N_3)_4Fe_2 + H_2O$, is obtained in a similar way to the other ferricyanides. It forms fine red monoclinic prisms, easily soluble in water and permanent in the air.

Lead Ferricyanide, $Pb_3(C_3N_3)_4Fe_2 + 16H_2O$, is formed by mixing hot solutions of the potassium salt and lead nitrate. It forms dark reddish-brown crystals slightly soluble in cold, and rather more soluble in hot water.

The ferricyanides of most of the other heavy metals are precipitates, some of which, like that of tin, are colourless; but generally possessing a yellow, greenish-brown, or red-brown colour.

FERROCYANIDES AND FERRICYANIDES OF IRON.

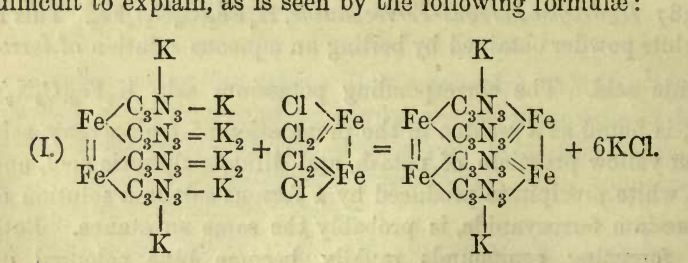
387 *Hydrogen Ferrous-Ferrocyanide*, $H_4\overset{iv}{Fe}_2(C_3N_3)_4\overset{iv}{Fe}_2$. This is a white powder obtained by boiling an aqueous solution of ferrocyanic acid. The corresponding potassium salt, $K_4\overset{iv}{Fe}_2(C_3N_3)_4\overset{iv}{Fe}_2$, is found as a residue in the preparation of hydrocyanic acid from yellow prussiate of potash, and dilute sulphuric acid, and the white precipitate produced by a ferrous salt in a solution of potassium ferrocyanide, is probably the same substance. Both the foregoing compounds rapidly become blue coloured on exposure to the air from absorption of oxygen. When the potassium salt is heated with dilute nitric acid the compound, $K_2\overset{vi}{Fe}_2(C_3N_3)_4\overset{iv}{Fe}_2 + 4H_2O$, is obtained, and this, when dried, forms a fine violet-blue powder which is transparent when seen in thin layers, allowing green light to pass through. When it is heated with a solution of the ferrocyanide the white salt is again obtained, and the solution contains ferricyanide of potassium:[1]

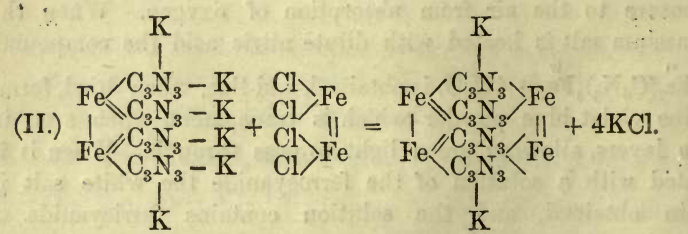
$$K_2\overset{vi}{Fe}_2(CN)_{12}\overset{iv}{Fe}_2 + K_8\overset{iv}{Fe}_2(CN)_{12} = K_4\overset{iv}{Fe}_2(CN)_{12}\overset{iv}{Fe}_2 + K_6\overset{vi}{Fe}_2(CN)_{12}.$$

Soluble Prussian Blue or *Ferric Potassium Ferrocyanide*, $K_2\overset{vi}{Fe}_2(C_3N_3)_4\overset{iv}{Fe}_2$. Ferric salts produce a blue precipitate in solutions of potassium ferrocyanide which is usually termed Prussian

[1] Williamson, *Mem. Chem. Soc.* iii. 125 (1846).

blue, and was formerly believed to be ferric ferrocyanide. A precipitate very similar to this, termed Turnbull's blue, and containing ferrous ferricyanide, is obtained when solutions of potassium ferricyanide and ferrous sulphate are mixed. The precipitates thus obtained always contain potassium, inasmuch as the above double salt is formed. It possesses the same composition as the above-named violet-blue compound, but possesses different properties, and it is obtained in the pure state by pouring solutions of the iron salts into an excess of ferrocyanide or ferricyanide. The precipitate is then well washed with water in order to remove potassium chloride until the wash-water is coloured blue. The residue then consists of soluble Prussian blue. It is perfectly soluble in pure water, yielding a dark blue liquid from which it is precipitated by the addition of salts. The fact that ferric salts produce with a ferrocyanide solution a precipitate having the same composition as that which is formed when a ferrous salt is added to a ferricyanide solution, is not difficult to explain, as is seen by the following formulæ:





The formulæ thus obtained are identical, inasmuch as it is immaterial which side of the compound contains the tetrad ferrous, or the hexad ferric group.[1] Soluble Prussian blue was first prepared from potassium ferrocyanide by Berzelius,[2] and Robiquet[3] observed that potassium forms an essential constituent, whilst Kekulé[4] was the first to propose the above

[1] Skraup, *Liebig's Annalen*, clxxxvi. 371.
[2] *Schweigg. Journ.* xxx. 34.
[3] *Ann. Chim. Phys.* xliv. 279.
[4] *Lehrb. Org. Chem.* i. 327.

formula. The truth of this, however, was ascertained by Reindel and Skraup, who showed that the precipitate obtained by ferricyanide and ferrous salt is identical with that obtained by ferrocyanide and ferric salt.

388 *Turnbull's Blue or Ferrous Ferricyanide,* $(\overset{vi}{Fe_2})_2(\overset{iv}{Fe_2})_3(C_3N_3)_8 = 2Fe_5(CN)_{12}$. This body was first prepared by Gmelin[1] by precipitating ferricyanide with ferrous sulphate. It was afterwards prepared on the large scale in England and named Turnbull's blue from the name of the supposed discoverer. Williamson[2] then showed that the precipitate thus obtained contains potassium, which can be removed by warming for some time with stannous chloride and subsequent washing with boiling water. The same compound is obtained by precipitating soluble Prussian blue with a ferrous salt. In the dry state it forms a beautiful blue powder, which has a copper-red lustre and contains a certain quantity of water. On heating hydrocyanic acid is evolved and ferric oxide is formed, and when boiled with caustic potash, ferrocyanide of potassium and black ferric hydroxide are formed:

$$Fe_5(CN)_{12} + 8KOH = K_8(CN)_{12}Fe_2 + Fe_3(OH)_8.$$

Insoluble Prussian Blue; Williamson's Blue, $(\overset{vi}{Fe_2})_4(\overset{iv}{Fe_2})_3(C_3N_3)_{12} = 2Fe_7(CN)_{18}$, is obtained, mixed with soluble Prussian blue, by pouring a solution of ferrocyanide of potassium into one of ferric chloride. By heating the precipitate for some time with ferric chloride the whole of the potassium may be removed. It is likewise obtained by oxidizing Turnbull's blue by treating it either with nitric acid or chlorine water (Williamson):

$$6Fe_5(CN)_{12} + Cl_6 = 4Fe_7(CN)_{18} + Fe_2Cl_6.$$

This substance is also formed by precipitating soluble Prussian blue with ferric chloride (Skraup), and forms in the dry state a deep blue powder which, on trituration, assumes a bright copper-like lustre. It always contains a certain quantity of water which cannot be driven off by heat, as decomposition then takes place with evolution of hydrocyanic acid and formation of ferric oxide. When heated strongly in the air Prussian blue burns like tinder, and when boiled with caustic potash, ferrocyanide and ferric hydroxide are formed:

$$2Fe_7(CN)_{18} + 24KOH = 3K_8(CN)_{12}Fe_2 + 4Fe_2(OH)_6.$$

[1] *Schweigg. Journ.* xxxiv. 325. [2] *Chem. Soc. Memoirs,* iii. 125.

Concentrated sulphuric acid converts it into a white pasty mass, neither hydrocyanic acid nor iron being removed. When dried in a vacuum on a porous plate an amorphous powder remains which is decomposed by water into Prussian blue and sulphuric acid (Berzelius). Commercial Prussian blue is obtained by precipitating a solution of ferrous salt with ferrocyanide of potassium. The more or less deeply coloured precipitate is then exposed to the air and treated with chlorine water, dilute nitric acid, or bleaching powder solution, and afterwards with hydrochloric acid in order to remove ferric oxide which is formed. It is a deep blue powder or mass which, when dried, possesses a conchoidal fracture and copper-like lustre. It always contains more or less potassium, and is a mixture of the three preceding compounds in varying proportions. Prussian blue dissolves in ammonium tartrate with a violet colour, and in oxalic acid with a beautiful blue colour. This latter liquid was formerly much used as a blue ink. It has, however, now been replaced by the violet and blue aniline colours.

The several blue compounds of cyanogen and iron all contain water, and are hygroscopic, and a part of this water is so firmly combined, that it is only given off at a temperature at which the salt decomposes.

Prussian Green, $(\overset{vi}{Fe_2})_6(\overset{iv}{Fe_2})_3(C_3N_3)_{16} = 2Fe_9(CN)_{24}$, is obtained as a green hydrated precipitate when an excess of chlorine is passed through a solution of the yellow or red prussiate and the liquid then heated to boiling and the precipitate boiled with hydrochloric acid (Pelouze). When the dry compound is heated to 180° cyanogen gas is evolved and a violet-blue compound is formed. Caustic potash decomposes Prussian green into ferric hydroxide and a mixture of the yellow and red prussiates:

$$2Fe_9(CN)_{24} + 30KOH = 3K_8(CN)_{12}Fe_2 + K_6(CN)_{12}Fe_2 + 5Fe_2(OH)_6.$$

A green body, having probably the same composition as Prussian green, is obtained by the continued action of oxidising agents on Williamson's blue.

A ferric salt of ferricyanic acid is not known in the solid state, for when ferric chloride is added to a solution of ferricyanide of potassium no precipitate occurs. The liquid, however, becomes of a dark-brown colour and probably contains the salt, $\overset{vi}{Fe_2}(C_3N_3)_4\overset{vi}{Fe_2}$.

NITRO-PRUSSIDES OR NITRO-FERRICYANIDES.

389 Leopold Gmelin and other chemists observed that the coffee-brown solution obtained by the action of nitric acid on yellow prussiate of potash yields a splendid purple-red colour in contact with sulphides of the alkalis. Playfair[1] showed in 1849 that this reaction is produced by the presence of a peculiar compound which is formed by the action of nitric acid upon the yellow or red prussiate. Nitro-prussic acid is obtained by passing nitric oxide into an acid solution of potassium ferrocyanide. Hydrogen ferricyanide is produced in the first instance:

$$H_8(CN)_{12}Fe_2 + NO = H_6(CN)_{12}Fe_2 + H_2O + N,$$

and this acts on the nitric oxide as follows:

$$H_6(CN)_{12}Fe_2 + 2NO = H_4(CN)_{10}(NO)_2Fe_2 + 2HCN.$$

Potassium nitro-prusside is also produced when the precipitate formed by the action of ferrous salt on potassium cyanide is treated with potassium nitrite:

$$K_2Fe_4(CN)_{10} + 2KNO_2 = K_4Fe_2(CN)_{10}(NO)_2 + 2FeO,$$

the ferrous oxide being thereby converted into ferric oxide and ammonia being liberated.[2]

In order to prepare the nitro-prussides, powdered yellow prussiate of potash is treated with double its weight of strong nitric acid which has been previously mixed with an equal volume of water. The coffee-coloured solution evolves carbon dioxide, cyanogen, nitrogen, and hydrocyanic acid, and probably also cyanic acid, derived from the oxidation of the hydrocyanic acid. As soon as the whole is dissolved it is warmed on a water-bath, the evolution of gas continuing until the solution is not coloured blue by ferrous sulphate, but a dark-green or grey precipitate falls down. On cooling, potassium nitrate crystallises out, from which the dark mother-liquor is poured off, saturated with sodium carbonate, and heated to the boiling point, when a green or brown precipitate is formed. This is removed by filtration, and the nitrates are again separated from the nitro-prussides by crystallisation. The solution can also be precipitated with sulphate of copper, and the bright green

[1] *Phil. Trans.* 1849, ii. 477. [2] Städler, *Zeitsch. f. Chem.* v. 559.

precipitate decomposed, after washing, by boiling with a soluble basic hydroxide and thus converted into soluble salts.

390 *Nitro-prussic acid,* $H_4(CN)_{10}(NO)_2Fe_2$, is formed by decomposing the silver salt with hydrochloric acid, or the barium salt with dilute sulphuric acid. The red strongly acid solution leaves on evaporation in a vacuum dark-red deliquescent prismatic needles. This compound is very unstable and partially decomposes during the concentration of the liquid with formation of ferric hydroxide, hydrocyanic acid, &c.

Potassium Nitro-prusside, $K_4(CN)_{10}(NO)_2Fe_2$, forms dark-red monoclinic prisms which deliquesce in the air and are readily soluble in water.

Sodium Nitro-prusside, $Na_4(CN)_{10}(NO)_2Fe_2+4H_2O$, crystallises most readily of all the nitro-prussides, and is usually prepared by concentrating the solution as above described until a sufficient quantity of nitro-prusside is crystallised out. This is then removed from the warm solution in order to avoid any admixture of nitrates. It is purified by crystallisation and forms large ruby-red rhombic prisms. It dissolves in 2·5 parts of water at 15° and is more soluble in hot water. When exposed to light, the solution decomposes with separation of Prussian blue and nitric oxide. Boiled with caustic soda ferrous hydroxide is separated, sodium ferrocyanide and sodium nitrate being formed:

$$6Na_4(CN)_{10}(NO)_2Fe_2 + 28NaOH = 2Fe(OH)_2 + 5Na_3(CN)_{12}Fe_2 + 12NaNO_2 + 12H_2O.$$

The nitro-prussides of ammonium and of the alkaline-earth metals also form red, easily soluble salts, their solutions decomposing on standing or on boiling with separation of Prussian-blue and ferric oxide. The silver salt and the ferrous salt are flesh-coloured precipitates.

The splendid purple colour which the nitro-prussides impart to a solution of an alkaline sulphide is very characteristic, and this reaction is employed for the detection of small quantities of alkalis and alkaline earths in solution by passing a little sulphuretted hydrogen through the liquid and then adding a few drops of nitro-prusside solution. This purple compound is very unstable, decomposing quickly with formation of hydrocyanic acid, ammonia, nitrogen, ferrocyanides, ferricyanides, &c.

When alcoholic solutions of sodium sulphide and sodium nitro-prusside are mixed this purple compound separates out in oily drops.

IRON THIOCYANATES.

391 *Ferrous Thiocyanate,* $Fe(SCN)_2 + 3H_2O$, is obtained in large pale-green monoclinic crystals by dissolving iron wire in concentrated thiocyanic acid and evaporating the liquid in absence of air. The salt dissolves readily in water, alcohol, and ether, and becomes red-coloured on exposure to the air.

Ferric Thiocyanate, $Fe_2(SCN)_6 + 3H_2O$. The blood-red colour produced when a soluble thiocyanate is brought into contact with a solution of a ferric salt depends on the formation of this compound, which is obtained in the pure state when a mixture in the right proportions of anhydrous ferric sulphate and potassium thiocyanate is treated with alcohol and the solution evaporated over sulphuric acid in a vacuum. Dark-red or almost black cubical crystals are deposited, and these dissolve readily in water, alcohol, and ether. If a concentrated aqueous solution be shaken with ether it becomes colourless and the ether attains a purple-red colour. On warming or diluting with water the aqueous solution becomes colourless with deposition of ferric hydroxide. The solution is also decolourised in presence of reducing agents as well as on treatment with mercuric chloride or gold chloride, inasmuch as the double thiocyanates are formed which are deposited as black crystalline precipitates.

IRON AND SULPHUR.

392 *Iron Monosulphide,* FeS, occurs as troilite in small quantities in many meteorites, and is easily formed by the direct union of the elements. Iron wire burns in sulphur vapour with a bright light, and a roll of sulphur penetrates red-hot wrought-iron and steel, but not cast-iron, with formation of the molten sulphide.[1] In order to prepare this substance a mixture of three parts of iron filings and two parts of sulphur is thrown gradually into a red-hot crucible. In this way a porous black mass is obtained which melts at a higher temperature, with separation of sulphur if any higher sulphides had been formed, but as a rule the artificial sulphide usually contains an excess of iron, and this is got rid of by heating with an excess of sulphur. For the preparation of

[1] Evain, *Ann. Chim. Phys.* xxv. 106.

the monosulphide Berzelius recommends the process proposed by Gahn, namely, to stir a white-hot rod of iron in molten sulphur. The sulphide which is formed fuses and falls to the bottom of the crucible. The operation is continued as long as any free sulphur remains. Pure monosulphide of iron is a yellowish crystalline mass having a metallic lustre, and sometimes crystallising in hexagonal prisms. It has a specific gravity of 4·69, is not magnetic, and does not lose sulphur when ignited in an atmosphere of hydrogen, or when heated in absence of air to whiteness. When heated in the air it oxidises, being converted partly into ferrous sulphate, whilst at a high temperature sulphur dioxide and ferric oxide are formed. Sulphide of ammonium precipitates sulphide of iron from solutions of ferrous salts as a black amorphous hydrated precipitate, whilst the same re-agent throws down from ferric salts a mixture of monosulphide and sulphur:

$$Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$

If seven parts of iron filings and four parts of sulphur be rubbed up to a paste with water a black sulphide is also produced with evolution of heat. In this form it oxidises very quickly in the air with increase of temperature which, when the mixture is in large quantity, may rise to incandescence. Hence, according to Lemery, artificial volcanoes may be formed if several pounds of the above mixture be buried in the earth. The black amorphous sulphide is also formed by the reduction of ferric oxide or its salts in presence of sulphates and decomposing organic matter. This is the cause of the black deposit found in drains as well as in the excrements when iron is used as a medicine.

Iron Sesquisulphide, Fe_2S_3, does not occur pure in the mineral kingdom, but probably forms a constituent of magnetic pyrites and copper pyrites. It is obtained by gently heating sulphur and iron together as well as by the action of sulphuretted hydrogen on ferric oxide at a temperature not above 100°. The sulphide obtained at a red-heat forms a yellow non-magnetic mass which has a specific gravity of 4·4 and is decomposed by dilute hydrochloric acid into sulphuretted hydrogen, ferrous sulphate and iron disulphide. This latter remains behind in the form of the sesquioxide, but in the moist state can be pressed to an impalpable powder (Berzelius).

Magnetic pyrites may be regarded as a compound of the two

preceding sulphides. Its composition varies between $5FeS + Fe_2S_3$ and $6FeS + Fe_2S_3$. It crystallises in hexagonal plates, usually, however, occurring in the massive state, having a brownish-yellow or brassy colour, and is attracted by the magnet, sometimes being itself magnetic. Its specific gravity varies from 4·4 to 4·7, and it frequently contains as much as 5·5 per cent. of nickel, this metal being obtained in America from this source in considerable quantities. Iron sesquisulphide forms compounds with the other sulphides.[1]

Potassium Ferric Sulphide, $K_2Fe_2S_4$, is obtained when iron filings, sulphur, and potassium carbonate are heated together, and the residue extracted with water. Purple-coloured glistening needle-shaped crystals are thus obtained which have a specific gravity of 2·863 and burn when heated in the air, but when ignited in a current of hydrogen are converted without change of form into the black compound $K_2Fe_2S_3$.

Sodium Ferric Sulphide, $Na_2Fe_2S_4 + 4H_2O$, is obtained in a similar way and forms brown microscopic needles.

Silver Ferric Sulphide, $Ag_2Fe_2S_4$, is a dark brownish-black crystalline power obtained by the action of silver nitrate solution on the potassium compound. It is decomposed by hydrochloric acid with evolution of sulphuretted hydrogen.

Iron Disulphide, FeS_2, occurs very widely distributed as iron pyrites. This mineral was known in early times, but was not distinguished from copper pyrites, both being known under the name of *πυρίτης*. Agricola considered these as two varieties of the same mineral.

Iron pyrites occurs in all geological formations, and usually crystallises in cubes or pyritohedrons, but also occurs in other forms and combinations of the regular system. It is frequently found in spherical, botryoidal, or stalactytic masses, being formed by the action of organic matter on water which contains iron in solution in the form of sulphates. Hence it is frequently found in peat and in crystalline masses often possessing the form of the original organic matter such as wood, roots, &c. It is likewise found in chalk cliffs, in similar concretionary forms. In the pure state iron disulphide has a brass-yellow colour, and a specific gravity of 5·185. It is very hard, giving sparks when struck with steel, for which purpose it was formerly employed. Iron disulphide also occurs as radiated pyrites and marcasite forming bright brass-coloured rhombic crystals having a specific gravity

[1] Schneider, *Pogg. Ann.* cxxxvi. 460; Preis, *Journ. pr. Chem.* cvii. 10.

of 4·68 to 4·85. This is also widely diffused, occurring in various forms, especially in lignite beds. Iron disulphide may be obtained artificially by gently heating the monosulphide with sulphur, or by passing sulphuretted hydrogen over the oxides or chlorides of iron heated to redness. When an intimate mixture of ferric oxide, sulphur, and sal-ammoniac is heated slowly above the temperature at which the latter compound volatilises the disulphide is obtained in small brass-yellow octohedrons and cubes (Wöhler). Crystalline pyrites is also formed when sulphide of carbon vapour acts upon heated ferric oxide (Schlagdenhauffen). Iron disulphide is not magnetic and is not attacked by dilute acids or sulphuric acid, but readily dissolves in nitric acid with separation of sulphur.

IRON AND NITROGEN.

393 *Iron Nitride*, Fe_2N. Berthollet noticed that when ammonia is passed over ignited iron wire it is converted into its elements and the iron becomes brittle. This depends upon the fact that at a low temperature iron nitride is formed, and this is decomposed again at a higher point. In order to prepare the nitride, ferrous or ferric chloride is heated to a temperature below redness in a current of dry ammonia. A silver-white brittle mass is thus obtained having a specific gravity of 5·0, and this when brought in the state of powder into a gas-flame ignites with emission of bright sparks. When heated in hydrogen pure iron is left. Iron nitride has a specific gravity of 6·03 and is so soft that it may be cut with a knife;[1] it is magnetic and oxidises very easily in the air, dissolving in nitric acid with evolution of nitric oxide, and also in dilute sulphuric acid with formation of hydrogen, nitrogen, ferrous sulphate, and ammonium sulphate. Aqueous vapour converts it at a red-heat into black magnetic oxide.

Another iron nitride, having the composition Fe_5N_2, occurs as a lustrous metallic deposit on the lavas of Etna. It may be artificially prepared by heating the lava in a current of hydrochloric acid and then leading ammonia over the strongly heated mass. It is likewise formed, although with greater difficulty, when the lava is ignited in a current of sal-ammoniac vapour.[2]

Iron Nitroso-thiocarbonate, $Fe_4CS_3(NO)_6 + 3H_2O$. This com-

[1] Stahlschmidt, *Pogg. Ann.* cxxv. 37. [2] Silvestri, *Pogg. Ann.* clvii. 165.

pound is formed when sodium nitrite and sodium thiocarbonate are added to a solution of ferrous sulphate.[1] The body thus obtained may be recrystallised from ether, forming black prisms which are soluble in alcohol and ether, and are not attacked by dilute acids and alkalis. On boiling with caustic alkali ammonia is evolved and ferric oxide deposited. Potassium cyanide converts it into potassium nitroprusside.

Iron Nitroso-sulphides. These compounds, discovered by Roussin,[2] are obtained when the nitrites and sulphides of the alkali metals act upon iron salts, in the same way as the nitroprussides are formed by the action of the nitrites and cyanides on iron compounds. The composition of these compounds has not been satisfactorily ascertained, although they have been analysed by several chemists.[3]

Iron Nitroso-sulphide, $Fe_3S_5H_2(NO)_4$ (Roussin); $Fe_3S_3(NO)_4 + 2H_2O$ (Proczinsky); $Fe_6S_5(NO)_{10} + 4H_2O$ (Rosenberg). This compound is obtained by gradually adding a solution of iron salt to a solution of potassium nitrite and ammonium sulphide. The mixture is then boiled for a few minutes and filtered; on cooling, the salt separates out in black metallic lustrous needles, soluble in 112 parts of cold and two parts of boiling water. Its solution possesses an intense dark blackish-brown colour and has a styptic taste. Alkalis and soluble sulphides and many other salts separate this compound from its solution, but on boiling with caustic potash iron oxide is separated and a *potassium iron nitroso-sulphide*, $Fe_2K_2S_3(NO)_4$ (Proczinsky), formed, which is deposited in black triclinic easily soluble crystals. Caustic soda yields a similar salt. Cyanide of potassium converts the nitro-sulphides into nitro-prussides.

IRON AND PHOSPHORUS.

394 In the year 1780, J. C. F. Meyer whilst examining the cause of the cold-shortness of iron came to the conclusion that this was produced by the presence of a peculiar metal to which he gave the name *hydrosiderum*. The subject was investigated shortly afterwards by Bergman, who found that when the residue obtained by dissolving cold-short iron in sulphuric acid, is fused

[1] Löw, *Pharm. Vierteljahrsb.* xiv. 375. [2] *Ann. Chim. Phys.* [3], lii. 285.
[3] Proczinsky, *Ann. Chem. Pharm.* cxxv. 302; Rosenberg, *Ber. Deutsch. Chem. Ges.* iii. 312.

before the blowpipe with reducing agents a metallic bead is obtained which he also believed to be a peculiar metal to which he gave the name of *siderum*. In 1784, Meyer repeated his experiments and came to the conclusion that the substance thus obtained was a compound of iron and phosphoric acid, and it was afterwards ascertained that the body got by reduction on charcoal is a phosphide of iron.

This compound, which has the composition Fe_2P, is obtained by fusing a ferrous or ferric phosphate together with lamp-black, under a layer of chloride of sodium. It is a porous, metallic, non-magnetic powder, which when heated in the air is converted into a basic phosphate, $Fe_4P_2O_{11}$. When ferrous sulphate solution is added to a hot mixture of caustic potash and phosphorus, iron phosphide, Fe_3P_2, is precipitated as a magnetic powder which takes fire when heated in the air to 100° (Schenck). If ferric phosphate be heated to whiteness in a current of hydrogen, the compound Fe_4P_3, is obtained as a metallic lustrous non-magnetic mass, and when iron pyrites or iron powder is ignited in a stream of phosphuretted hydrogen a grey non-magnetic powder, having the composition Fe_3P_4 is obtained, whilst the compound FeP is prepared as a dark-grey powder when the monosulphide is ignited in the same gas, or when iron is heated in phosphorus vapour. These various phosphides of iron do not undergo alteration in the air. They dissolve in hot hydrochloric acid with formation of hydrogen phosphide and phosphoric acid, and they can be fused in all proportions with iron. Probably some of the above compounds, as well as others which have been prepared, are mixtures of phosphide with metallic iron.[1]

IRON AND ARSENIC.

395 When metallic iron is ignited with an excess of arsenic in the absence of air a white and very brittle mass of FeAs is obtained. Lölingite or $FeAs_2$ occurs as a mineral crystallised in silver-white rhombic prisms. Mispickel or arsenical pyrites Fe_2AsS_2 is a more common mineral; it crystallises in short rhombic prisms of a silver-white colour. A portion of the iron is frequently replaced by cobalt, and this mineral serves as the chief source of the arsenical compounds.

[1] Freese, *Pogg. Ann.* cxxxii. 225.

Detection and Estimation of Iron.

396 The ferrous salts, as has been stated, readily absorb oxygen, and their solutions, therefore, usually contain larger or smaller quantities of the ferric salts. Hence they give a bluish-white precipitate with ferrocyanide of potassium, and this on shaking with air assumes a dark-blue colour. Ferricyanide of potassium produces at once a dark-blue precipitate, whilst the ferric salts are coloured a dark-brown by this reagent, no precipitate being formed. By these reactions it is easy to ascertain whether a ferrous, or a ferric salt, or a mixture of both, is contained in solution.

With alkalis, ferrous salts give a white, or usually greenish precipitate which quickly changes to a dark-green colour on exposure to air, and afterwards becomes brown. Ferric salts give at once a brown precipitate. The presence of these latter may also be readily ascertained by the blood-red colour which they produce with soluble thiocyanates. A bead of microcosmic salt or borax is coloured dark green by ferrous salts. This colour readily changes to a yellow or reddish-brown by oxidation. On cooling, the colour becomes less distinct, disappearing altogether if only traces of ferric oxide are present. Iron can also be detected in the dry way by Bunsen's test. For this purpose the compound is heated on the end of a carbonized wooden match, which has previously been impregnated with fused sodium carbonate, held in the reduction zone of the non-luminous gas-flame. The whole is then rubbed up in an agate mortar with a little water, the particles of iron being extracted on the point of a magnetised knife-blade. The adhering particles of finely-divided iron are brought on to a small piece of filter paper, dissolved in a drop of aqua regia and a drop of potassium ferrocyanide added, this confirmatory test being necessary inasmuch as nickel and cobalt are also magnetic metals.

The iron compounds do not impart any colour to the non-luminous gas-flame. Ferric chloride gives a characteristic spark spectrum consisting of three groups of lines with the following wave-lengths:—

$$\alpha \text{ (Fraunhofer's E)}. \begin{cases} 5326 \\ 5269 \\ 5231 \end{cases} \quad \beta \begin{cases} 4959 \\ 4923 \end{cases} \quad \gamma \begin{cases} 4406 \\ 4383 \end{cases}$$

When traces of chlorine are present only the last group is seen. The spark spectrum of the metal contains many hundred bright lines of which each has a corresponding dark line in the solar spectrum. The most distinctly marked and brightest are:

In the indigo (very bright)	4414·7 4404·2 4382·8
Fraunhofer's G . .	4307·2
„ E . .	5269·5 5268·5
„ b_3 . .	5168·3
„ b_4 . .	5166·7

It has already been stated that manganese is obtained together with iron in the course of qualitative analysis and the mode of their separation has already been described. The precipitate containing ferric hydroxide may also contain uranium. This is readily separated by digesting the precipitate with concentrated solution of ammonium carbonate. The washed residue is then dissolved in hydrochloric acid and the confirmatory test for iron applied.

In the processes of *quantitative analysis* iron is determined both gravimetrically and volumetrically. In the first case the iron must be present as ferric salt. Ferrous salts are, therefore, previously oxidised by nitric acid and then precipitated by ammonia, the precipitate washed with boiling water, dried, ignited, and weighed as the sesquioxide. If the solution should contain tartaric acid, sugar, or other organic compounds, ammonia produces no precipitate. If, on the other hand, phosphoric or boric acid be present, the ferric salts of these acids are thrown down. In these cases the iron must be previously precipitated as sulphide; this is well washed, dissolved in nitric acid and the iron precipitated by ammonia. If other metals precipitable by ammonia and sulphide of ammonium be present, the iron can be separated by adding acetate of soda to the neutral solution and boiling, when basic ferric acetate is thrown down. This is filtered whilst boiling, washed with boiling water, dried, and ignited, and weighed as ferric oxide. The precipitate may contain alumina, and this must then be separated by means of caustic potash. Iron is separated from manganese by precipitation with the succinate or benzoate of ammonium. The precipitate is first washed with water and then with ammonia, when it is converted into ferric hydroxide.

For *volumetric determination* iron must be present as a ferrous salt. According to Marguerite's process, a standard solution of potassium permanganate is added to a solution of the ferrous salt containing free sulphuric acid. As soon as a permanent red colouration is noticed the oxidation is complete, and the quantity of iron is calculated from the following equation:

$$10FeSO_4 + 9H_2SO_4 + 2KMnO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 2KHSO_4 + 8_2HO.$$

In order to determine the strength of the permanganate solution pure ammonium ferrous sulphate is employed, $FeSO_4 + (NH_4)_2SO_4 + 6H_2O$, seven parts by weight of the salt containing exactly one part of iron.

Penny's method depends upon the fact that a ferrous solution containing a free acid is oxidised to ferric salt by potassium dichromate as follows:

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O.$$

The completion of the reaction is ascertained by bringing a drop of the solution in contact with a solution of red prussiate of potash on a porcelain plate, when no further blue colour should be observed. These volumetric methods are in daily use in iron-works for testing the value of the ore and for analysing the various products of the manufacture. As many of the ores of iron are ferric compounds they must be converted into ferrous salts. This is done by warming the acid solution in a current of carbon dioxide in contact with pure zinc. In the laboratory the volumetric method is also frequently employed, as it not only is a quick and accurate method, but also because the amount of ferrous salt in the presence of ferric salt can thus be ascertained. For this purpose it is only necessary to treat the original solution with the standard permanganate and afterwards to reduce another sample of the liquid with zinc. By this method likewise the tedious separation of alumina and ferric oxide may be avoided, inasmuch as both may be weighed together, then brought into solution, and this, after the reduction of the iron, treated by the volumetric method.

Marguerite's method does not give good results in the presence of hydrochloric acid, inasmuch as chlorine is in this case evolved. Hence if this acid be present it is either necessary to remove it by boiling with sulphuric acid, or Penny's method must be employed.

The *atomic weight* of iron has been accurately determined by several chemists. Svanberg and Norlin,[1] by the oxidation of iron with pure nitric acid, obtained the number 55·83 as the mean of seven experiments; and the same chemists by reducing the oxide in hydrogen obtained the number 55·95 also as a mean of seven experiments. Berzelius found the number 56·191 as a mean of two experiments by oxidising the metal with nitric acid, and Erdmann and Marchand,[2] who reduced the oxide in hydrogen, obtained the number 55·89 as a mean of eight experiments. Maumené[4] dissolved pure iron wire in nitric acid and precipitated with ammonia, the mean of six experiments giving the number 55·96; and, lastly, Dumas,[3] by the analysis of ferric chloride, obtained the number 56·06, whilst by the analysis of ferrous chloride the number 55·96 was obtained.

COBLAT. Co = 58·6.

397 The word cobalt occurs in the writings of Basil Valentine as well as in those of Paracelsus and Agricola; two meanings were attached to this name; in the first place it signified a sprite or goblin supposed to haunt the mine, whilst in the second place it was used to denote certain minerals, which are, however, too imperfectly described for exact identification. But it appears that in this latter sense it was employed to designate minerals which, although they possessed the appearance of a well-known metallic ore, did not yield any of this metal when subjected to the usual treatment. Hence the word came to signify a false ore. In later times the same name was given to the mineral which was used for the purpose of colouring glass blue, and is still employed for the preparation of smalt. In 1735, Brandt stated that the blue colouring of smalt depends upon the presence of a peculiar metal to which he gave the name kobalt-rex, and in 1742 he showed that the colour of smalt does not depend, as had been believed, upon the presence of arsenic and iron, metals which are usually found in cobalt ores, for he found that some of these ores occur free from arsenic, and that these likewise gave the blue colour. The new metal was stated to be magnetic and extremely infusible. These observations were confirmed by

[1] *Ann. Chem. Pharm.* l. 432.
[2] *Ann. Chem. Pharm.* l. 442.
[3] *Journ. Pr. Chem.* xxxiii. 1.
[4] *Ann. Chim. Phys.* [3], xxx. 380.
[5] *Ann. Chim. Phys.* [3], lv. 129.

Bergman in 1780, and the compounds of cobalt were afterwards examined by many chemists.

Cobalt does not occur in the free state in nature and its ores are not very widely distributed. It is found as linnaeite Co_3S_4; skutterudite $CoAs_3$; speiss-cobalt $(CoNiFe)As_2$; glance-cobalt $(CoFe)(AsS)_2$; earthy cobalt or wad $(CoMn)O,2MnO_2 + 4H_2O$; erythrine or cobalt-bloom $Co_3(AsO_4)_2 + 8H_2O$, &c.

Cobalt is likewise almost always found as a constituent of meteoric iron, and its presence has been detected in the solar atmosphere.

Treatment of Cobalt Ores. For the preparation of cobalt compounds speiss-cobalt or other arsenical ores are employed. These, after roasting or calcination in the air, yield an impure cobalt arsenate which comes into commerce under the name of *zaffre*, and which is further worked up as hereafter described. The cobalt ores, however, usually contain large quantities of nickel and iron as well as other metals, and for this reason they are usually smelted in order to get rid of the greater part of the iron, the process employed being similar to that which is used for the extraction of copper. The roasted ore is fused with a flux of carbonate of lime or sand, when the iron slag flows on to the surface whilst the cobalt remains below as a heavy *speiss* or stone. The roasted ore or the speiss is then dissolved in strong hydrochloric acid, any arsenate of iron which may be present being precipitated by the careful addition of bleaching-powder solution and a small quantity of milk of lime; the clear supernatant liquid is drawn off, treated with sulphuretted hydrogen for the purpose of separating copper, bismuth, &c., and then the oxide of cobalt is precipitated from the clarified solution by bleaching-powder. The oxide thus obtained is washed and ignited, and this is brought into market and largely used for colouring glass and porcelain as well as for the preparation of the chloride and nitrate of cobalt. This oxide usually contains iron and almost always nickel and other impurities. The processes of separating these will be described later on.

398 *Preparation of Metallic Cobalt.* The metal is obtained as a grey powder by igniting the oxide or chloride in a current of dry hydrogen. By strongly heating the oxalate under a layer of powdered glass the metal can be obtained as a coherent mass, and this may be fused to a regulus by heating it in a crucible made of lime, magnesia, or graphite. Cobalt possesses the colour of polished iron; it is, however, harder than this

metal, although it melts at a somewhat lower temperature. It is malleable and very tough; it is also magnetic and has a specific gravity varying from 8·5 to 8·7. Cobalt in the form of powder absorbs oxygen from the air, often with ignition; the compact metal however does not undergo change at the ordinary temperature, but slowly oxidises when heated and burns at a very high temperature with a red flame.

It is readily soluble in hydrochloric, dilute sulphuric, and nitric acids, and, at a red-heat, decomposes steam.

COBALT AND OXYGEN.

Two oxides of cobalt are known—

Cobalt monoxide, CoO.
Cobalt sesquioxide, Co_2O_3.

399 *Cobalt Monoxide, or Cobaltous Oxide*, CoO. This compound is obtained by reducing the higher oxide by heating it either in a current of hydrogen to a temperature not above 350° (Winkelblech) or in a current of carbon dioxide to redness until its weight is constant (Russell).[1] It is a light-brown or greenish-brown powder, which does not alter in the air.

Cobaltous Hydroxide, $Co(OH)_2$, is obtained by precipitating a cobaltous salt with caustic potash in the absence of air. A blue basic salt is first obtained, and this, on boiling, is quickly converted into a rose-red coloured hydroxide. It absorbs oxygen from the air and changes to a brown tint.

Cobaltous-Cobaltic Oxide, Co_3O_4. This compound, which corresponds to the magnetic oxide of iron, is obtained when one of the other oxides or the nitrate is heated in the air; thus obtained, it forms a black powder having a specific gravity of about 6·0. If a dry mixture of sal-ammoniac and cobalt oxalate or cobalt chloride be heated in the air, or in oxygen, this compound is obtained in hard, metallic-lustrous, microscopic octohedrons, which are not magnetic. It is obtained in the hydrated state by the oxidation of moist cobaltous hydroxide in the air.

If either of the oxides already mentioned, or the carbonate, be fused with caustic potash in the air, and the temperature increased to the point at which the alkali volatilises,

[1] *Chem. Soc. Journ.* xvi. 51.

thin six-sided graphitic scales are formed. These are insoluble in water but are decomposed by hydrochloric acid with evolution of chlorine, and by nitric acid with evolution of oxygen. The composition of this compound, to which the name of *potassium cobaltate* has been given, has not yet been ascertained with certainty; it approaches, however, to the formula [1] $Co_9O_{16}K_2 + 3H_2O$.

Cobaltic Oxide or Cobalt Sesquioxide, Co_2O_3, is a dark-brown powder formed by gently igniting the nitrate.

Cobaltic Hydroxide, $Co_2(OH)_6$, is prepared by precipitating a cobalt salt with an alkaline hypochlorite solution. It forms a brownish-black powder, which is decomposed by hydrochloric acid with evolution of chlorine, and by oxyacids with evolution of oxygen.

The sesquioxide and its hydroxide act, therefore, as peroxides, but at the same time they possess weak basic properties inasmuch as they dissolve in well cooled acids with a brownish-yellow colour. The most stable of these compounds is a strongly coloured solution obtained by dissolving the hydroxide in acetic acid; this decomposes only when heated.

COBALTOUS SALTS.

400 These correspond to the monoxide. In the anhydrous state they possess a deep violet or blue colour, and in the hydrated condition a faint rose-red tint. If a dilute solution of the chloride be used as an ink the writing is not visible when it is allowed to dry in the air, but, on warming, the characters appear of a bright blue colour, disappearing again gradually on standing in the air owing to the absorption of moisture.

From this property the cobalt salts have long been employed for the manufacture of the so-called *sympathetic inks*, by which is understood any liquid the writing of which is invisible under ordinary conditions but which can be rendered apparent by some simple treatment. The first attempt at the preparation of such an ink depended upon the fact that a solution of lead acetate becomes black when treated with a decoction of orpiment in milk of lime. These two liquids, which were known as "aquæ magneticæ e longinquo agentes," were mentioned by

[1] Schwarenberg, *Ann. Chem. Pharm*, cxvii. 211; Pebal, *ibid.* c. 262; Mayer, *ibid.* c. 226.

Lemery in 1681 as "encres appellées sympathiques." Soon after this other sympathetic inks were made known in the treatise termed *The Key to unlock the Cabinet of the Secrets of Nature*, published in 1705; and the method for preparing a sympathetic ink from certain bismuth ores is described. Up to the year 1744 the peculiar properties of this ink were believed to be due to bismuth, but in that year Gessner proved that cobalt contained in these ores was the active agent in the production of the ink. This property of the cobalt salts to change colour from rose to blue on loss of water has lately been applied to the construction of floral hygrometers. Artificial flowers are prepared, the petals of which are tinted with cobalt salts. In damp weather the flower is pink, in dry weather violet or blue. This invention is, we need scarcely add, a Parisian one.

The soluble normal cobaltous salts possess an acid reaction and a sour, astringent taste.

Cobalt Chloride, $CoCl_2$. Powdered metallic cobalt takes fire when warmed in chlorine gas, forming blue crystalline scales of the anhydrous chloride, which can be readily sublimed in a current of chlorine. They dissolve in alcohol with a blue colour and on addition of water first become violet, and then rose-coloured. Cobalt chloride is obtained in aqueous solution by dissolving the carbonate, or one of the oxides, in hydrochloric acid; short dark-red monoclinic prisms crystallise on cooling the concentrated warm solution; these possess the composition $CoCl_2 + 6H_2O$ and have a specific gravity of 1·84; they melt at 86°·7 to a blue liquid which begins to boil at 111°, gradually losing two molecules of water and depositing peach-coloured deliquescent crystals $CoCl_2 + 4H_2O$: these again when heated to 121° yield a dark crystalline powder $CoCl_2 + 2H_2O$. A concentrated solution of the chloride becomes blue on addition of concentrated sulphuric or hydrochloric acid.

Cobalt Bromide, $CoBr_2$. If bromine vapour be passed over metallic cobalt at a dark red-heat, a green fused mass is formed which absorbs water from the air, yielding a dark-red liquid. This solution is also obtained by bringing cobalt, bromine and water together; if the solution be allowed to stand over sulphuric acid, dark red prisms having the composition $CoBr_2 + 6H_2O$ are deposited, and this when heated to 100° gives a purple mass containing $CoBr_2 + 2H_2O$, which at 130° yields the anhydrous bromide as an amorphous green mass (Rammelsberg, Hartley).

Cobalt Iodide, CoI_2. This substance is formed with evolution of heat when finely divided cobalt is gently warmed with water and iodine. If the solution be allowed to evaporate over sulphuric acid until crystals begin to deposit, the hydrate $CoI_2 + 2H_2O$ is formed, which on exposure to the air deliquesces to a red liquid. This when heated to 100° until it turns green deposits dark-red prisms $CoI_2 + 6H_2O$; which at 130° lose their water and the anhydrous iodide remains as an iodine-like mass.

Cobalt Fluoride, CoF_2, is obtained by dissolving the oxide or carbonate in hydrofluoric acid; on evaporation rose-red crystals are deposited having the composition $CoF_2 + 2H_2O$: these are decomposed by boiling water with the formation of a light-red insoluble oxy-fluoride.

Cobalt Sulphate, $CoSO_4 + 7H_2O$. This salt occurs native as cobalt vitriol, or bieberite, in crystalline crusts. It is prepared artificially by dissolving the carbonate or oxides in dilute sulphuric acid; and crystallises in red prisms having the form of iron vitriol which are unalterable in the air. It has a specific gravity of 1·924 (Schiff), possesses a weak astringent metallic taste, is easily soluble in water, but does not dissolve in alcohol. According to Tobler 100 parts of water dissolve:

At	10°	20°	29°	50°	70°
$CoSO_4$	30·5	36·4	40	55·2	65·7

When its solution is allowed to stand at from 40° to 50° monoclinic crystals having the composition $CoSO_4 + 6H_2O$ are formed, and these are isomorphous with the corresponding zinc salt. If a concentrated solution of cobalt sulphate be poured gently into sulphuric acid a peach-blossom coloured powder $CoSO_4 + 4H_2O$ is deposited. All the hydrates lose their water on heating but do not fuse, becoming opaque and of a rose-red colour (Proust).

Cobalt Nitrate, $Co(NO_3)_2 + 6H_2O$. This substance generally forms an indistinctly crystalline mass: it may be obtained by slow evaporation in monoclinic prisms, having a specific gravity of 1·83 and not undergoing change in dry air. It begins to melt below 100°, and when more strongly heated the violet liquid becomes thick and green; then it begins to boil, giving off nitrous fumes, and the black oxide is left behind.

Phosphates and Arsenates of Cobalt. The normal and monohydrogen cobalt salts of the different modifications of phosphoric acid are rose-red or violet-blue insoluble compounds. The

di-hydrogen-orthophosphate is easily soluble in water and forms a gummy mass. The arsenates are similar bodies; the normal arsenate $Co_3(AsO_4)_2 + 8H_2O$ occurs native as cobalt-bloom or erythine, in violet monoclinic needles isomorphous with vivianite or in earthy masses. Zaffre is also an impure basic arsenate $(CoO)(AsO_4)_2$ obtained by roasting cobalt glance free from iron, or by dissolving the ore in nitric acid and precipitating with soda. This is also used for painting on porcelain.

401 *Silicates of Cobalt. Smalt.* The silicates of cobalt do not occur as minerals in nature. Although certain specimens of ancient Egyptian glass have been found to be coloured blue by cobalt, the direct application of the ores of cobalt for this purpose appears to date from the 16th century. Smalt is a potash-glass intensely coloured blue by cobalt oxide. Up to the middle of this century smalt was largely used for colouring starch, paper, &c., but the recent introduction of artificial ultramarine has done much to diminish the demand for cobalt blue.

For the preparation of smalt, the ore such as speiss-cobalt or cobalt-glance, free from iron and sulphur, is first carefully roasted so that the cobalt is mainly oxidised, whilst nickel, iron, copper, and bismuth remain as much as possible unaltered and separate out when the mixture is melted with glass as an insoluble speiss. The roasted ore is then fused with a mixture of quartz-sand, and potashes, the fusion being effected in large earthen pots, arranged in a furnace similar to that employed for the manufacture of plate-glass. The arsenides of nickel and iron sink to the bottom of the pot and the glass is ladled out into cold water. The blue glass is then ground with water to an impalpable powder under granite stones.

Smalt varies in composition according to the differences in the ores, as also in the proportion of sand and potashes employed. Thus the amount of silica varies between 56 and 70 per cent., that of potash between 12 and 22, and that of cobalt between 6 and 16 per cent. In addition, smalt contains small quantities of alumina, ferric oxide, and frequently also lime and oxide of lead; the commoner varieties likewise contain oxide of nickel. Smalt has the advantage as a paint over ultramarine that its colour is not destroyed by the action of acids.

Together with smalt, two other pigments containing cobalt must be mentioned although their composition is undetermined.

Rinmann's Green is obtained either by precipitating a mixture of zinc sulphate and cobalt sulphate with soda and heating

the washed precipitate, or by evaporating a solution of cobalt nitrate with oxide of zinc, or zinc nitrate, to dryness, and igniting the residue. Recently a very intense green coloured mass has been obtained by heating zinc white with roseo-cobaltic chloride [1] (see page 137) to a moderate red-heat.

Thénard's Blue or Cobalt Ultramarine. When alumina, or a salt of aluminium, is strongly heated with cobalt oxide or one of its salts, a fine blue-coloured compound is obtained. This is prepared on the large scale by heating a mixture of alumina with phosphate or arsenate of cobalt; it is used as a paint.

Carbonates of Cobalt. The normal salt, $CoCO_3$, is obtained as a bright-red powder, consisting of microscopic rhombohedrons, by heating cobalt chloride to 140° with a solution of sodium bicarbonate saturated with carbon dioxide. The salt $CoCO_3 + 6H_2O$ is formed by allowing mixed solutions of cobalt nitrate and sodium bicarbonate saturated with carbon dioxide to stand exposed to a low temperature until the amorphous precipitate which is first formed becomes crystalline; the dry salt is converted into the anhydrous salt on warming. When a cold or hot solution of a cobalt salt is precipitated with normal or acid sodium carbonate, bluish or violet basic cobalt carbonates of varying composition, are thrown down.

Cobaltous Cyanide, $Co(CN)_2$. This is a red precipitate obtained when solutions of potassium cyanide and a cobalt salt are brought together. It easily dissolves in excess of the precipitant forming the soluble double salt, $Co(CN)_2 + 2KCN$. If the solution be treated with dilute hydrochloric acid cobaltous cyanide is again precipitated, but if the solution be previously diluted this does not occur, inasmuch as potassium cobalti-cyanide is formed (see page 140).

COBALTIC SALTS.

402 Cobalt sesquioxide possesses very feebly basic properties. It dissolves in cold acids yielding brown coloured solutions, and the compounds thus obtained decompose with great ease, the oxy-salts evolving oxygen, and the chloride chlorine. The most stable salt is the acetate, and this is obtained when moist cobaltic hydroxide is added to cold acetic acid. The dark yellowish-brown solution gives brown precipitates with alkalis and sodium

[1] *Ber. Entw. Chem. Ind.* i. 875.

phosphate, and yields a black precipitate with ammonium sulphide.

In addition to these unstable simple cobaltic salts, a number of other remarkable compounds are known which contain the hexad group Co_2. These are far more stable than the simple salts, and exhibit altogether distinct reactions.

Potassium Cobalt Nitrite, $K_6Co_2(NO_2)_{12} + 3H_2O$, was discovered by Fischer,[1] and is obtained as a yellow precipitate when the solution of a cobaltous salt, acidified with acetic acid, is mixed with a solution of potassium nitrite:

$$2CoCl_2 + 10KNO_2 + 4HNO_2 = K_6Co_2(NO_2)_{12} + 4KCl + 2NO + 2H_2O.$$

As this salt is somewhat soluble in water, it is best to wash it with a solution of potassium acetate, and then with an 80 per cent. alcohol. Cobalt yellow, as this compound is also termed, is a bright yellow powder consisting of microscopic pyramids, or of four- or six-sided stellated forms. According to Sadtler[2] the salt is usually anhydrous. It can however be obtained, according to the concentration of the solution, with from one to four molecules of water, and its colour then varies from a bright yellow to a dark greenish-yellow. It is decomposed by nitric and hydrochloric acids, but only when heated. Caustic potash solution attacks it with difficulty. Caustic soda or baryta water on the other hand, decomposes it readily, on gently warming, with precipitation of the brown hydroxide. The salt suspended in water is only slowly attacked by sulphuretted hydrogen, but sulphide of ammonium instantly separates black sulphide of cobalt.

Corresponding compounds of sodium, ammonium, and thallium are also known.

If a solution of cobalt chloride be precipitated with potassium nitrite without addition of acid, a yellow hydrated precipitate of potassium cobaltous nitrite, $2KNO_2 + Co(NO_2)_2$, is obtained, soluble in hot water and yielding a red solution.[3]

[1] *Pogg. Ann.* lxxiv. 124. [2] *Sillim. Journ.* [2], xlix. 189.
[3] Erdmann, *Journ. Prac. Chem.* xcvii. 385.

Ammoniacal Cobalt Compounds or Cobaltamine Salts.

403 In 1799 Tassaert[1] observed that a solution of a cobalt salt in ammonia assumes a brown colour on exposure to the air, and that this changes on boiling to a wine-red, whilst Thénard[2] in 1803, stated that these changes were brought about by an absorption of oxygen. This latter observation was confirmed by Proust, who found that on evaporating the solution, black cobaltic oxide separates out. The compounds which are thus formed have attracted the attention of many chemists,[3] but still the subject cannot be considered to have been yet exhausted. For although the examination of these bodies began in the year 1851, the constitution of these peculiar ammoniacal cobalt compounds is far from being understood. They all possess the empirical composition of one molecule of a cobaltic salt, such as Co_2Cl_6, combined with several molecules of ammonia. We are not only acquainted with normal, acid, and basic salts of this description, but also with some which contain several acid radicals. Many of these form double salts with the chlorides of platinum, gold, and other metals; whilst others again exist which although possessing identical chemical composition exhibit a difference in properties, or are isomerides. The double salts possess a purely saline taste as opposed to a metallic one, and in some of the groups the corresponding hydroxides are known in aqueous solution. These hydroxides exhibit an alkaline reaction, and have a purely alkaline taste.

The cobaltamine salts are all characterised by peculiar colours, and their names are derived from this property. The following is the series of the normal chlorides:

Hexammonio-cobaltic (or dichro-cobaltic) chloride, $Co_2Cl_6(NH_3)_6$.
Octammonio-cobaltic (or praseo-cobaltic) chloride, $Co_2Cl_6(NH_3)_8$.
Decammonio-cobaltic (or roseo- and purpureo-cobaltic) chloride, $Co_2Cl_6(NH_3)_{10}$.
Dodecammonio-cobaltic (or luteo-cobaltic) chloride, $Co_2Cl_6(NH_3)_{12}$.

Dichro-cobaltic Chloride, $Co_2Cl_6(NH_3)_6 + 2H_2O$. This is obtained when an ammoniacal solution of cobaltic chloride is exposed

[1] *Ann. Chim.* [1], xlii. 211.
[2] *Ibid.* [1], xxviii. 95, 106.
[3] Genth, *Ann. Chem. Pharm.* lxxx. 275; Fremy, *Compt. Rend.* xxxii. 509 and 808; Claudet, *Phil. Mag.* iv. [2], 253. A history of these compounds will be found in *Untersuchungen d. Ammoniakalische Kobalt Verbindungen*, by Fr. Rose. Heidelberg: 1871.

to the air until flocculæ of cobaltic hydroxide separate out. The solution is then treated with an excess of hydrochloric acid and allowed to stand for some time. It is thus obtained in the form of feather-like crystals, which when thin possess a reddish-brown colour; on the other hand, when crystallised from neutral solutions it is deposited in connected plates consisting of hexagonal pyramids, and these when small transmit dark green light, whilst when of a larger size they are black and opaque. The peculiar dichroism of this salt is well seen under the microscope. If a crystal be broken up the splinters exhibit different colours. The salt dissolves in pure water with a greenish-blue colour, which soon becomes of a light blue and passes gradually into violet. On heating, these changes occur at once, and, on boiling, a black precipitate of cobaltic hydroxide is formed and ammonia is evolved (Rose).

Praseo-cobaltic Chloride, $Co_2Cl_6(NH_3)_8 + 2H_2O$. This is usually formed together with the foregoing compound and other cobaltamine chlorides. It crystallises in small glistening needles which possess an emerald green colour. These dissolve in water yielding a green solution which soon becomes red, and undergoes decomposition on boiling. If fuseo-cobaltic chloride be warmed with tolerably dilute hydrochloric acid a deep violet solution is obtained, and this on cooling deposits small violet octohedrons which posesss the same composition as the green salt, and pass into the latter when dissolved in concentrated sulphuric acid, to which hydrochloric acid is gradually added.[1]

Fuseo-cobaltic salts. Fremy has described a series of salts which likewise contain eight molecules of ammonia to two atoms of cobalt. These may be considered as basic praseo-cobaltic salts. Thus the nitrate is $Co_2(NO_3)_4(OH)_2(NH_3)_8 + 2H_2O$. The fuseo-salts are contained in the brown solution which is formed when an ammoniacal solution is exposed to the air. They are precipitated from this solution by alcohol and are non-crystallisable.

404 *Roseo-cobaltic Salts.* These are usually formed when the oxidised solution is slightly acidified, and likewise when solutions of the fuseo-salts are warmed. They possess a dark-red or cherry-red colour, are dichroic, and their solutions are easily decomposed on boiling.

Roseo-cobaltic Hydroxide, $Co_2(OH)_6(NH_3)_{10}$, is obtained when a solution of the chloride is decomposed by silver oxide, or that of

[1] Vortmann, *Ber. Deutsch. Chem. Ges.* 1877, 1451.

the sulphate by baryta water. The red solution has a strongly alkaline taste, it absorbs carbon dioxide from the air, and on heating decomposes with separation of cobaltic hydroxide.

Roseo-cobaltic Chloride, $Co_2Cl_6(NH_3)_{10} + 2H_2O$, is contained in the solution when it becomes red on exposure to the air. When this is treated with hydrochloric acid in the cold this chloride is separated out in the form of a brick-red precipitate, and this is washed with concentrated hydrochloric acid and ice-cold water, and dried at as low a temperature as possible. It dissolves in water with a red colour, the solution passing after a time to a violet-red colour, and containing purpureo-cobaltic chloride. It forms a double salt with platinum chloride, $Co_2Cl_6(NH_3)_{10} + 2PtCl_4 + 5H_2O$, which is deposited as a pale yellowish-red crystalline powder.

Roseo-cobaltic Nitrate, $Co_2(NO_3)_6(NH_3)_{10} + 2H_2O$, is prepared from cobalt nitrate in the same way as the last compound is obtained from the chloride. It is deposited on spontaneous evaporation of the wine-red solution in red monoclinic crystals.

Roseo-cobaltic Sulphate, $Co_2(SO_3)_3(NH_3)_{10} + 5H_2O$. This separates out from the dark-red ammoniacal solution on the addition of sulphuric acid as a brick-red crystalline powder. Garnet-red quadratic crystals may be obtained by recrystallising from a slightly acidified aqueous solution.

405 *Purpureo-cobaltic Salts* are formed when the corresponding roseo-cobaltic compounds are gently heated with acids. They have a violet or purple colour, and the sulphate yields with baryta-water a deep red strongly alkaline solution of the corresponding hydroxide.

Purpureo-cobaltic Chloride, $Co_2Cl_6(NH_3)_{10}$, is obtained, by boiling a solution of the roseo-salt, in the form of a carmine precipitate which is very difficultly soluble in water, and crystallises from a hot dilute hydrochloric acid solution in anhydrous quadratic prisms. It forms with platinum chloride the double salt, $Co_2Cl_6(NH_3)_{10} + 2PtCl_4$, which is almost insoluble in cold water, and is thrown down in brownish-red crystals having a silky lustre.

The purpureo-cobaltic salts are distinguished from their isomerides, the roseo-cobaltic compounds, not only by their colour, but also by the fact that whilst the first are usually anhydrous the latter are, as a rule, hydrated. The purpureo-salts can also be crystallised from aqueous solution without previously passing into the roseo-salts. They may, however, be

indirectly combined with water. Thus if an ammoniacal solution of purpureo-chloride be dissolved in cold strong hydrochloric acid, hydrated roseo-chloride is obtained, and this on heating, even in dilute acid solution, again loses water and passes into the purpureo-compound. Roseo-cobaltic chloride dissolves at 10° in 4·8 parts, whilst purpureo-cobaltic chloride dissolves only in 287 parts of water.

406 *Luteo-cobaltic Salts* frequently occur as products of the decomposition of the other cobaltamine compounds. They are tolerably stable, possess a more or less yellow or bronze colour and exhibit dichroism. When the sulphate is decomposed by baryta-water a strongly alkaline yellow solution of the hydroxide, $Co_2(OH)_6(NH_3)_{12}$, is obtained.

Luteo-cobaltic Chloride, $Co_2Cl_6(NH_3)_{12}$, is obtained when the ammoniacal cobalt chloride solution is allowed to stand for some time, especially in the presence of sal-ammoniac. The formation of the salt is facilitated by addition of oxidising substances such as lead dioxide, bromine, &c. (Braun, Mills). It crystallises in reddish-yellow monoclinic prisms or pyramids, which dissolve slowly in cold but readily in hot water. It forms a difficultly soluble double salt with platinum chloride, which crystallises from hot solution in monoclinic prisms having the composition $Co_2Cl_6(NH_3)_{12} + 3PtCl_4 + 21H_2O$.

Ammonio-cobaltous Salts are formed as the last product of the action of oxygen on the ammoniacal cobalt solutions. They are slightly soluble in ammonia and are decomposed by water with evolution of oxygen (Fremy). The nitrate, $Co_2O_2(NO_3)_4(NH_3)_{10} + 2H_2O$, is obtained when a rapid current of air is passed through a solution in ammonia of cobalt nitrate and ammonium nitrate. Dark olive-green prisms separate from the brown solution on standing, and these are soluble in hot ammonia and may be recrystallised. Hot water decomposes them with evolution of 5·2 per cent. of oxygen.

407 *Nitro-Cobaltamine Salts.* These salts are obtained by the action of nitrous acid or the nitrates on ammoniacal cobalt solutions. They may be classed in three groups, one or other of which is obtained according to the conditions of the experiment. The chlorides have the following composition:

Croceo-cobaltic chloride, $Co_2Cl_2(NO_2)_4(NH_3)_8$.
Xantho-cobaltic chloride, $Co_2Cl_4(NO_2)_2(NH_3)_{10}$.
Flavo-cobaltic chloride, $Co_2Cl_2(NO_2)_4(NH_3)_{10}$.

The Croceo-cobaltic Salts may be regarded as purpureo-cobaltic salts in which two-thirds of the acid radical is replaced by nitroxyl. The *sulphate*, $Co_2SO_4(NO_2)_4(NH_3)_8$, is formed when a mixture of solutions of cobalt sulphate and potassium nitrite saturated with ammonia is exposed to the air. It is deposited in orange-yellow crystals together with green cobaltic hydroxide. The mixture is filtered and the residue dissolved in hot dilute nitric acid, and from this solution the sulphate is obtained on cooling in the form of yellow quadratic tables. Large wine-red crystals are also obtained from dilute solutions. It is slightly soluble in boiling water.[1]

Croceo-cobaltic Chloride, $Co_2Cl_2(NO_2)_4(NH_3)_8$, is obtained by heating the sulphate with a solution of barium chloride and hydrochloric acid. It is somewhat more soluble than the sulphate and forms sherry-coloured iridescent tables. It yields a double salt with platinum chloride, $Co_2Cl_2(NO_2)_4(NH_3)_8 + PtCl_4$, crystallising in dark-orange prisms.

Xantho-cobaltic Salts may be considered as roseo-cobalt compounds in which nitroxyl replaces one-third of the acid radical. The *sulphate*, $Co_2(SO_4)_2(NO_2)_2(NH_3)_{10}$, is formed by passing nitrous fumes through an ammoniacal solution of cobalt sulphate, the solution being kept alkaline by the addition of ammonia (Gibbs and Genth). The brown-red liquid deposits crystals on spontaneous evaporation which may be recrystallised from acetic acid solution. It forms brownish-yellow rhombic tables which dissolve with difficulty in cold water, and when boiled with hydrochloric acid the salt yields a purpureo-cobaltic chloride.

Xantho-cobaltic Chloride, $Co_2Cl_4(NO_2)_2(NH_3)_{10}$, is obtained by decomposing the sulphate with barium chloride, when it is deposited in well-formed brownish-yellow beautifully iridescent crystals. Hot hydrochloric acid decomposes it like the sulphate. The platinum double salt has the composition $Co_2Cl_4(NO_2)_2(NH_3)_{10} + 2PtCl_4 + 2H_2O$; it is almost insoluble in water and is deposited from dilute hydrochloric acid solution in brown crystals.

The Flavo-cobaltic Salts may be considered as roseo-cobalt compounds in which two-thirds of the acid radical is replaced by nitroxyl.

Flavo-cobaltic Chloride, $Co_2Cl_2(NO_2)_4(NH_3)_{10}$, is obtained in dark-orange coloured crystals when a hot solution of purpureo-

[1] Gibbs, *Sillim. Journ.* [3], vi. 116.

cobaltic chloride is added to a solution of sodium nitrite slightly acidified with acetic acid.[1] It is easily soluble in hot water, and on the addition of silver nitrate yields xantho-cobaltic nitrate :

$$Co_2Cl_2(NO_2)_4(NH_3)_{10} + 4AgNO_3 = Co_2(NO_3)_4(NO_2)_2(NH_3)_{10} + 2AgCl + 2AgNO_2.$$

With platinum chloride and other chlorides it forms well crystallised double salts. The flavo-cobaltic salts are distinguished from the xantho-cobaltic salts, inasmuch as they yield flocculent precipitates with cyanides of the alkali-metals and the nitrates of platinum, nickel, cobalt, and cadmium.

COBALTICYANIDES.

408 *Potassium Cobalticyanide*, $K_6(CN)_{12}Co_2$, is formed when an excess of potassium cyanide is added to a solution of a cobalt salt, together with a little acetic acid or hydrochloric acid and the liquid well boiled:

$$6KCN + 2Co(CN)_2 + 2HCN = K_6(CN)_{12}Co_2 + H_2.$$

This salt is obtained in bright yellow crystals isomorphous with potassium ferricyanide.[2] Copper sulphate yields a blue, and silver nitrate a white precipitate, the salts $Cu_3(CN)_{12}Co_2$ and $Ag_6(CN)_{12}Co_2$ being formed. Ferrous cobalticyanide, $Fe_3(CN)_{12}Co_2$ is a white precipitate whilst cobaltous cobalticyanide, $Co_3(CN)_{12}Co_2 + 14H_2O$, is a bright red precipitate which becomes anhydrous and blue when heated to 200°. When the copper salt is decomposed by sulphuretted hydrogen *cobalticyanic acid*, $H_6(CN)_{12}Co_2$, is formed, and this is deposited in colourless silky needles on evaporating the solution. It is deliquescent, has a strongly acid taste and reaction, and is not attacked even by strong nitric acid.

COBALT AND SULPHUR.

409 *Cobalt Monosulphide*, CoS, is obtained as a black hydrated precipitate when a solution of a cobalt salt is mixed with ammonium sulphide. It dissolves in concentrated hydrochloric acid with evolution of sulphuretted hydrogen. The cold dilute acid

[1] Gibbs, *Ber. Deutsch. Chem. Ges.* iii. 43.
[2] Gmelin, *Handbuch Org. Chem.* i. 397.

dissolves it but slowly, whilst it is almost insoluble in dilute acetic acid. When the monosulphide is mixed with sulphur and the mixture ignited in a current of hydrogen the following sulphides are formed according to the temperature employed: CoS_2, Co_2S_3, CoS; and at a white heat, Co_2S (H. Rose). The monosulphide is found as an Indian mineral known as syepoorite, occurring in ancient schists in grains or veins of a yellowish steel-grey colour.

Cobalt pyrites or linnaeite, Co_3S_4, occurs at Bastnäs, near Riddarhyttan, at Müssen in Prussia, as well as at Mineral Hill in Maryland, and at Mine La Motte in Missouri. It forms steel-grey or tarnished copper-red regular octohedrons, and also occurs in the massive state. It usually contains more or less nickel as well as some iron and copper. The same compound can be artificially obtained as a blackish-grey powder by heating a cobalt salt with potassium polysulphide to a temperature of 160°.

COBALT AND PHOSPHORUS.

410 When pieces of phosphorus are thrown on to ignited cobalt a metallic lustrous blueish-white brittle mass is formed. This tarnishes on exposure to air and melts at a lower temperature than cobalt and contains 6 per cent. of phosphorus. On heating it burns with formation of a dark-blue glass (Pelletier). When cobalt reduced in hydrogen is heated to dark redness in the vapour of phosphorus, a light grey metallic lustrous mass is formed, containing 28·4 per cent. of phosphorus (Schrötter), and this corresponds nearly to the formula Co_3P_2, and this compound is also formed as a black powder by igniting a normal phosphate in a current of hydrogen.

COBALT AND ARSENIC.

411 *Cobalt Arsenide*, $CoAs_3$, occurs as skutterrudite near Modum in Norway crystallised in octohedrons or combinations as well as in the massive state. It possesses a colour from tin-white to a pale lead-grey, and usually contains small quantities of iron and sulphur.

Smaltite or tin-white cobalt, $CoAs_2$, usually contains varying

quantities of iron and nickel, and it occurs in tin-white octohedrons or combinations as well as in the massive state in the Erzegebirge.

Cobaltite, cobalt-glance, or bright white cobalt, $CoAs_2 + CoS_2$, crystallises in the regular system usually in pyramid octohedrons and their combinations, and a portion of the cobalt is usually replaced by iron. It has a silver-white colour inclining to red, and occurs at Tunneberg and other localities in Sweden, at Siegen in Westphalia, and the Bottolack Mine near St. Just in Cornwall. The most productive mines are those of Vena in Sweden, where it is found in mica-slate.

Detection and Estimation of Cobalt.

412 This metal is characterised by its black sulphide insoluble in acetic and dilute hydrochloric acids and by the fine blue colour which its compounds impart to the borax bead. If a cobalt compound be reduced on a carbonised match the metal is obtained in shining white magnetic particles, which dissolve in hydrochloric acid with a rose-red colour, the solution becoming blue on evaporation.

In the separation from other metals, already described under manganese (see p. 25), cobalt and nickel are always obtained together. The separation of these two will be described under the detection of nickel.

Cobalt chloride imparts to the non-luminous gas flame an evanescent rose-red colour, but this does not give any characteristic spectrum. The spark spectrum of the chloride contains a large number of bright lines of which the most important are the following (Lecoq de Boisbaudran):

α 5535 β 5265 γ 4868.

The metal also gives a spark spectrum consisting of a large number of bright lines of which the following in the blue are the most characteristic (Thalén):

{4867, 4839} {4813·5, 4791·7} 4778·7

Cobalt is usually estimated as the oxide, Co_3O_4. It may also be weighed as metal obtained by the reduction of the nitrate or the chloride in hydrogen; and when it is combined with a volatile acid it may be determined as the anhydrous sulphate by heating the salt with sulphuric acid.

The atomic weight of cobalt has been repeatedly determined but without concordant results. Rothhoff[1] converted a weighed quantity of the monoxide into the chloride and obtained the number 58·79. The relation between the carbon and cobalt in the oxalate gave Schneider[2] the number 59·85. Marignac,[3] by the analysis of the sulphate, obtained numbers varying from 58·49 to 58·61, whilst by the analysis of the anhydrous chloride he obtained similarly 58·57 to 58·69, and by that of the crystallised chloride 58·69 to 58·87. From numerous analyses of the cobaltamine salts Gibbs[4] deduced the number 58·85 as an average, whilst Dumas,[5] from the analysis of the chloride, obtained the number 58·85 to 59·03. Russell,[6] in fifteen closely agreeing experiments, obtained the number 58·6 by reducing the monoxide in a current of hydrogren. By dissolving the pure metal in hydrochloric acid and determining the amount of hydrogen evolved he likewise obtained the number 58·61 as a mean of four determinations.[7]

NICKEL, Ni. = 58·6.

413 The first mention of an ore of this metal is found in the writings of Hiarni in 1694, under the name of kupfer-nickel, this name, signifying false copper, being given to it because, whilst possessing the colour of a copper ore, this latter metal could not be extracted from it. In spite of the failure, the ore was long supposed to contain copper, but after the discovery of cobalt many believed that this metal was contained in kupfer-nickel.[8] In 1751 Cronstedt published in the Transactions of the Stockholm Academy an investigation upon an ore which was obtained from the mines of Helsingland. This yielded a green vitriol which imparted a brown and not a blue colour to glass, and yielded a hard brittle metal. In 1754 he stated that a semi-metal occurred most abundantly in kupfer-nickel, and therefore he proposed to give to it the name of nickel. He likewise showed that the speiss formed in the preparation of smalt consists to a large extent of nickel and was not, as had been believed, a burnt cobalt which had lost its spirit. Cronstedt's views did not find general acceptance, but in 1774 Bergman's

[1] *Pogg. Ann.* viii. 185.
[2] *Ibid.* ci. 387.
[3] *Arch. Phys. Nat.* [2], i. 373.
[4] *Sillim. Journ.* [2], xxv. 483.
[5] *Ann. Chim. Phys.* [3], lv. 129.
[6] *Journ. Chem. Soc.* [2], i. 51.
[7] *Chem. News*, xx. 20.
[8] See Link, *Phil. Trans.* 1726, p. 236.

research on nickel made its appearance, and in this he showed that the nickel which Cronstedt had only obtained in the impure state was in reality a new metal.

Nickel almost always occurs in nature together with cobalt. Its most important ores in addition to those which have already been described are nickeline or kupfer-nickel, NiAs, the most important ore of the metal found, in the Saxon mines, in Styria, at Leadhills, and in Connecticut; nickel-glance, $Ni(AsS)_2$; breithauptite, NiSb; millerite or nickel-blende, NiS; linnaeite, $(CoNiFe)_3S_4$; pentlandite, (NiFe)S; nickel-ochre or annabergite, $Ni_3(AsO_4)_2 + 8H_2O$; rewdanskite, $(NiFeMg)_3Si_2O_7 + 2H_2O$, &c. Nickel also occurs frequently in magnetic pyrites, that from the Gap Mine in Pennsylvania containing 5·6 per cent., and being worked for nickel. An important new source of nickel has lately been opened out in New Caledonia, where large quantities of a silicate of nickel called garnierite, $2(NiMg)_5Si_4O_{13} + 3H_2O$, occur.

Nickel is an essential constituent of meteoric iron, and its presence in extra-terrestrial matter was first detected by Prout. It is also contained in the sun's atmosphere.

414 The preparation of metallic nickel was formerly conducted by roasting and calcination. By this means nickel, cobalt, and copper, combined with arsenic and sulphur, are obtained in the form of a speiss, whilst the oxidised iron floats off as a slag. The speiss when fused with white sand yields smalt and a speiss free from cobalt, and this latter, when roasted, yields an impure oxide of nickel which may afterwards be reduced by means of carbon to the metallic state.

A purer product is obtained by separation in the wet way. For this purpose a matt containing nickel and cobalt is also prepared. This is then roasted and the crude oxides dissolved in hydrochloric or sulphuric acid. If the solution should contain ferrous salts these must be oxidised with bleaching powder, and the iron precipitated by the addition of lime or chalk, whilst the copper is thrown down with sulphuretted hydrogen or sodium sulphide. The cobalt is then precipitated by bleaching-powder, and the nickel contained in the clear solution precipitated as the hydroxide or carbonate by milk of lime or soda-ash. This is then ignited and purified by treatment with hydrochloric acid when the excess of lime and calcium carbonate dissolve. If calcium sulphate should be present, the impure oxide is heated with steam, and soda-ash solution added in such quantity

that after boiling for a quarter of an hour an excess still remains. The sodium sulphate is then removed by washing with water and the calcium carbonate (formed by double decomposition) dissolved in dilute hydrochloric acid. Cobalt and nickel can also be separated by adding ammonium sulphate to a concentrated solution of the mixed sulphates together with a small quantity of sulphuric acid when the difficultly soluble ammonium-nickel sulphate separates out, and this only requires to be heated in earthenware tubes in order to volatilise the ammonium sulphate which may thus be regained for further operations. The residual nickel sulphate can be almost completely reduced to oxide by roasting with a small quantity of charcoal. In order to remove the least traces of sulphur the residue is ignited with soda and saltpetre and afterwards well washed. The oxide is then pressed into the form of small cubes, and these strongly ignited with charcoal powder. The reduction takes place from the outside, the metal absorbing carbon. The operation is usually carried on in clay crucibles standing on the hearth of a reverberatory furnace, or in a special furnace invented by Künzel[1] which permits the reduction to be carried on continuously. This consists of a furnace through which vertical fire-clay tubes pass; these tubes are charged at the top with the mixture of crude oxide and coal, and the metal is withdrawn from time to time at the bottom. Commercial nickel contains carbon as well as small traces of cobalt, copper, iron, and other impurities.

The ore from New Caledonia, which is quite free from cobalt, may be worked up by two processes; according to the first, the ore is treated with hydrochloric acid, and the solution precipitated with oxalic acid, the insoluble oxalate being then reduced to metal by reduction with lime and carbon. Or the hydrochloric acid solution of the ore is heated with chalk to throw down oxides of iron and aluminium, and the nickel precipitated in the filtrate with a mixture of milk of lime and bleaching-powder.

In order to prepare the pure metal the oxalate may be ignited in absence of air and the metallic powder obtained fused in a double lime crucible (Deville), or the chloride may be reduced in a current of hydrogen.

415 *Properties.* Nickel is a lustrous silver-white metal having a steel-grey tinge. It is very hard and takes a fine polish, and

[1] *Bericht. Entw. Chem. Ind.* i. 866.

may easily be rolled out into thin plates and drawn into wire. Its specific gravity is 8·9. It is malleable and can be welded. When the metal contains carbon it is less malleable and more readily fusible than when it is pure. Nickel oxidises only with difficulty even on heating in the air, and melts at a somewhat lower temperature than iron and cobalt. It decomposes steam very slowly at a red-heat with formation of the monoxide, and it is soluble in hydrochloric or dilute sulphuric acid, and does not dissolve quickly even in the concentrated acid. On the other hand, it dissolves readily in dilute nitric acid; but if it be dipped into the concentrated acid it becomes "passive" as iron does. Nickel is attracted by the magnet and readily assumes a polar condition.

Electro-nickel Plating. Pure nickel is used as the positive pole in processes of the galvanic deposition of nickel which are especially valuable for coating iron and steel with a thin film of pure nickel. If the coating be well deposited it scarcely undergoes any oxidation. The process of nickel-plating was first applied to fire-arms in order to preserve them from rusting. Now, however, it is also used for covering various parts of machines, locks, keys, surgical instruments, and other fine iron- and steel-work, and is especially carried on in America. A great variety of proposals have been made for the preparation of the liquid used in this process, but the only bath which is practically useful is one made of pure nickel ammonium sulphate which is saturated at a temperature of from 20° to 25°.[1]

Alloys of Nickel.

416 In 1825 Thénard in his *Traité de Chimie* remarked that nickel was not employed for any practical purpose, although Engeström had pointed out so long ago as 1776, that Chinese packfong is an alloy of copper, zinc, and nickel. Packfong, or rather Pack-Tong means white copper, and Tong-Pack probably means the same thing, although in Europe this name changed to tomback is employed to describe a particular kind of brass. Since the middle of the last century a white alloy has been prepared at Suhl, in Hanneberg, from old copper slag, and Brandes in 1823 showed that this white copper chiefly consists of an alloy of copper and nickel, and thus commenced the manufacture of nickel alloys known under the name of German-

[1] *Ber. Entw. Chem. Ind.* i. 874.

silver, nickel-silver, or argentan, a trade which has now attained large dimensions. The nickel industry received a further impulse from the application of copper-nickel alloys to the manufacture of small coin, which was first introduced into Switzerland in 1850. The Swiss pieces of twenty, ten, and five centimes contain respectively fifteen, ten, and five per cent. of silver alloyed with 10 parts of nickel and 12·5 of zinc, the residue being made up of copper. These proportions are, however, not constant, as in the melting, more or less zinc volatilises. A yellow alloy containing twelve of nickel to eighty-eight of copper was adopted in 1856 by the United States Government for the one cent pieces, and in 1860 the Belgian Government instituted a nickel-copper coinage, containing twenty-five of the former to seventy-five of the latter metal, this same alloy being adopted in 1866 by the United States, for the five and ten cent pieces, and by Brazil in 1872. The German Government in 1873 adopted the same alloy for the five- and ten-pfennig pieces, and the pence and half-pence lately coined for Jamaica possess the same composition.

The advantages of nickel coining are, in the first place, that the metal is more valuable than copper, and, therefore, for the same value the coins can be of smaller size; secondly, that the alloy is hard and, therefore, the coin wears well; thirdly, that the alloy requires experienced workmen to prepare in the homogeneous condition; and, lastly, that in consequence of its hardness it requires powerful machinery for its manufacture. Owing to these uses of the metal the price of nickel suddenly rose, but has lately fallen again.

It is a very remarkable fact that a coin of the Bactrian King Euthydemos who reigned about 235 before Christ, analysed by Flight[1] possesses a very similar composition to the alloy in question:

Copper	77·58
Nickel	20·04
Cobalt	0·54
Iron	1·05
Tin	0·04
Silver	trace
Sulphur	0·09
	99·34

[1] The *Numismatic Chronicle*, viii. 305: and *Pogg. Ann.* cxxxix 507.

The above alloys of nickel absorb on fusing a considerable quantity of gases, and the more the higher the temperature and the percentage of nickel contained. Künzel found that if an alloy of eighty of copper and twenty of nickel be fused in a crucible half filled with the mixture, and this quickly cooled the mass froths up from the evolution of gas, and runs over the top of the crucible. If a copper-nickel alloy be granulated in water yellow globules are obtained, and these are frequently so thin that they swim on the surface of the water.[1]

Nickel-silver, or *German-silver* is an alloy of copper, nickel, and zinc, containing its constituents in varying proportions according to the method of preparation and the articles for which it is used. As a rule five parts of copper, two of nickel, and two of zinc are used, thus giving rise to an alloy which has the appearance of silver alloyed with one quarter of copper. In Sheffield eight parts of copper, 3·5 of zinc, and three of nickel are employed. A commoner and yellowish alloy is obtained when less nickel is used, whereas if more nickel be employed the alloy has a bright white colour, and takes a high silvery polish. The addition of 2·5 per cent. of iron makes the alloy whiter, but also harder and more brittle.

The following table gives the composition of several of these alloys: No. I. is Chinese packfong analysed by Fyfe; II. the same by Kefferstein; III. German-silver by Bolley; IV.—VI. various samples of nickel-silver used in Birmingham for articles to be plated, and analysed by Louyet; and VII. an alloy from Sheffield distinguished by extraordinary elasticity and used for the friskets of printing-presses, analysed by Elsner.

	I.	II.	III.	IV.	V.	VI.	VII.
Copper .	40·4	26·3	54·0	63·34	62·40	62·63	57·4
Zinc . .	25·4	36·8	28·0	17·01	22·15	26·05	25·0
Nickel .	31·6	36·8	18·0	19·13	15·05	10·85	13·0
Iron . .	2·6	—	—	trace	trace	trace	3·0
	100·0	99·9	100·0	99·48	99·60	99·53	98·4

In preparing nickel-silver it is usual to melt the zinc with half the weight of copper which it is ultimately to contain, this alloy being then cast into thin plates. The other half of the copper is then fused with the nickel under a bed of charcoal-powder, and the copper zinc alloy added. After cooling, the

[1] *Ber. Entw Chem. Ind.* i. 867.

alloy possesses a crystalline structure, and this is got rid of by hammering and rolling, again heating, and allowing it to cool. When it has once lost its crystalline structure it can be worked like brass, and although it is harder and tougher it may be rolled out to foil and drawn to wire. Hence it is used for a great number of purposes, as it is much cheaper than silver and less apt to be discoloured. On the other hand, it is more readily attacked by acid liquids, and for this reason nickel-silver articles employed for household use are generally covered with a coating of silver.

NICKEL AND OXYGEN.

417 *Nickel Monoxide*, or *Nickel Oxide*, NiO. This substance occurs as bunsenite at Johanngeorgenstadt in Saxony, in vitreous translucent pistachio-green regular octohedrons having a specific gravity of 6·398. It may be obtained in the form of a green crystalline powder by strongly heating the hydroxide, carbonate or nitrate. If nickel borate be ignited with lime in a pottery furnace and the mass treated with hydrochloric acid, nickel oxide remains behind in green cube-octohedrons which have a specific gravity of 6·8 (Ebelmen), whilst if the metal be ignited in a current of steam, pale olive-green crystals of the oxide are formed.

Nickel Hydroxide, $Ni(OH)_2$, is thrown down when a solution of a nickel salt is heated with potash or soda, as an apple-green precipitate slightly soluble in water. It dissolves in ammonia with a blue colour, and it separates out as a green crystalline powder on boiling the ammoniacal solution.

Nickel Sesquioxide, or *Nickel Peroxide*, Ni_2O_3, is a black powder obtained by gentle ignition of the nitrate or carbonate in the air. It dissolves in sulphuric and nitric acids with evolution of oxygen, and in hydrochloric acid with evolution of chlorine, whilst nitrogen is evolved when it is acted upon by ammonia:

$$3Ni_2O_3 + 2NH_3 + 3H_2O = 6Ni(OH)_2 + N_2.$$

If chlorine be passed through the hydroxide suspended in water, nickel perhydroxide or nickel sesquihydroxide, $Ni_2(OH)_6$, is obtained

$$3Ni(OH)_2 + Cl_2 = NiCl_2 + Ni_2(OH)_6.$$

This compound is formed as a black precipitate when the solution of a nickel salt is warmed with an alkaline hypochlorite solution. On drying it forms a black mass with lustrous conchoidal fracture. Acids and ammonia act upon it as upon the sesquioxide.

SALTS OF NICKEL.

418 These salts are derived from the monoxide. In the anhydrous condition they are usually yellow-coloured, whilst in the hydrated state and combined with colourless acids they possess an apple-green to an emerald-green colour. The soluble normal salts have a slightly acid reaction and a sweetish astringent metallic taste and act as emetics.

Nickel Chloride, $NiCl_2$. Finely-divided nickel burns with a bright light when it is slightly heated in dry chlorine gas, forming yellow scales resembling Mosaic gold. If a solution of the oxide or carbonate in hydrochloric acid be evaporated to dryness the anhydrous chloride is obtained as a yellow earthy mass which readily dissolves in water with evolution of heat. On gently heating for some time in the air it evolves chlorine leaving a residue of the oxide. In absence of air, on the other hand, it can be sublimed, and is then obtained in golden scales which when boiled for some time with caustic potash are completely decomposed into the hydroxide. They become gradually coloured green on exposure to the air owing to the absorption of moisture, and then are easily soluble in water. The salt $NiCl_2 + 6H_2O$ is obtained in short six-sided prisms on concentrating the solution; these are easily soluble in water and in alcohol. The anhydrous chloride of nickel absorbs ammonia at the ordinary temperature, swelling up to a white powder, possessing a slightly violet tinge, and having the composition $NiCl_26NH_3$. The same compound is obtained in blue octohedrons by dissolving the chloride in ammonia and allowing the solution to cool. This salt readily evolves ammonia when exposed to the air. It is easily soluble in water, but less so in strong alcohol.

Nickel Bromide, $NiBr_2$. Finely-divided nickel absorbs bromine vapour when heated in it, becoming incandescent. In absence of air, the bromide sublimes in golden scales which deliquesce on exposure. The solution, which is also obtained by bringing the

metal in contact with bromine and water, gives on evaporation deliquescent needles of $NiBr_2 + 3H_2O$.

Nickel Iodide, NiI_2. If nickel powder reduced in hydrogen be heated with iodine, or if the hydroxide be dissolved in hydriodic acid, the solution evaporated to dryness in absence of air, and the solid heated, nickel iodide sublimes in iron-black scales. The solution when evaporated to a syrup deposits bluish-green very deliquescent prisms having the composition $NiI_2 + 6H_2O$.

Nickel Fluoride, NiF_2, is obtained by dissolving the hydroxide or carbonate in hydrofluoric acid, and evaporating, when blue-green crystals of $NiF_2 + 3H_2O$ separate. These are decomposed by boiling water with formation of an insoluble pale green oxyfluoride.

Nickel Sulphate, $NiSO_4$. This salt was first obtained in the pure and crystalline condition in 1775 by Bergman. In order to prepare it, nickel or its hydroxide or carbonate is dissolved in dilute sulphuric acid. When the solution contains an excess of acid and at the ordinary temperature, the salt, $NiSO_4 + 6H_2O$, separates in hard bluish-green quadratic pyramids. At a temperature of from 50° to 70° green monoclinic crystals of the same composition separate out and these become bluish and opaque when allowed to stand at the ordinary temperature. When the salt crystallises from aqueous solution at from 15° to 20°, green rhombic prisms isomorphous with magnesium sulphate, and having the composition $NiSO_4 + 7H_2O$, are deposited. This salt is also known as nickel vitriol, or morenosite, occurring in acicular crystals, and also as a fibrous efflorescence on certain nickel ores. Crystallised sulphate of nickel when heated to 100° leaves the salt $NiSO_4 + H_2O$ as a powder, and this loses the whole of its water above 280°. One hundred parts of water dissolve (Tobler):

At	2°	16°	23°	41°	50°	60°	70°	
$NiSO_4$	30·4	37·4	41·0	49·1	52·0	57·2	61·9	parts.

The anhydrous sulphate absorbs ammonia, becoming strongly heated and increasing in bulk, forming a violet-white powder having the composition $(NiSO_4)6NH_3$. On dissolving the sulphate in strong ammonia and cooling, or allowing it to evaporate over sulphuric acid, transparent dark-blue quadratic prisms crystallise out having the composition $(NiSO_4)4NH_3 + 2H_2O$.

Ammonium Nickel Sulphate, $(NH_4)_2SO_4 + NiSO_4 + 6H_2O$. This salt is employed in the process of nickel-plating. It is obtained by dissolving nickel, free from iron and copper, in dilute sulphuric acid, and adding ammonium sulphate to the concentrated acid solution. The crystalline paste which is deposited is washed with cold water and purified by recrystallisation. It crystallises in short monoclinic prisms. One hundred parts of water dissolve (Link):

	At	3·5°	16°	20°	30°	40°	50°	68°	85°	
$(NH_4)_2SO_4 + NiSO_4$		1·8	5·8	5·9	8·3	11·5	14·4	18·8	28·6	parts.

The salt is almost insoluble in an acidified solution of ammonium sulphate (Thomson).

Nickel Nitrate, $Ni(NO_3)_2 + 6H_2O$, crystallises in green monoclinic tables which dissolve in two parts of cold water, and effloresce on exposure to dry air, deliquescing however in moist air, and being soluble in alcohol.

Nickel Nitrite, $Ni(NO_2)_2$, is obtained in solution by the decomposition of the sulphate with barium nitrite. It is a very unstable compound forming with potassium nitrite the easily soluble double salt $4KNO_2 + Ni(NO_2)_2$. This is obtained in brownish-red octohedrons by mixing a concentrated solution of the nitrite with an excess of potassium nitrite. When potassium nitrite is added to a nickel solution containing a calcium salt, a yellow crystalline precipitate of $2KNO_2 + Ca(NO_2)_2 + Ni(NO_2)_2$ is formed, which possesses great similarity to potassium cobaltic nitrite (see p. 134) and if a solution contain a sufficient quantity of calcium together with nickel and cobalt, the whole of the nickel, as well as the cobalt, may be thrown down by potassium nitrite. This fact must be remembered in the separation of the two metals.

The Phosphates of Nickel are insoluble in water, and more or less soluble in the mineral acids. The *arsenates* possess similar properties, and some of them occur in the mineral kingdom.

The Nickel Silicates also occur in nature. Rewdanskite is the most important. This mineral occurs at Rewdansk in the Urals, and is worked for nickel. It is an earthy mineral which chiefly consists of $(NiFeMg)_3Si_2O_7 + 2H_2O$, and contains about 18 per cent. of nickel. Noumaeite $2(NiMg)_5SiO_{13} + 2H_2O$ has lately been found in New Caledonia, and is now largely worked up for nickel in France. It contains 24 per cent. of nickel (Liversidge).

Nickel Carbonate, $NiCO_3$, is obtained, in the form of pale-green

microscopic rhombohedrons, by heating nickel chloride solution with calcium carbonate to 150°. When a nickel nitrate solution is mixed with solution of sodium bicarbonate saturated with carbon dioxide, and this allowed to stand at a low winter temperature, microscopic monoclinic crystals of $NiCO_3 + 6H_2O$ are formed, and these lose their water readily on warming. When a nickel solution is precipitated with an alkaline carbonate, basic salts of varying composition are thrown down in the form of pale green precipitates.

Nickel Cyanide, $Ni(CN)_2$, is an apple-green precipitate easily soluble in an excess of potassium cyanide with formation of the crystalline double salt, $Ni(CN)_2 + 2KCN$. This is again decomposed by dilute acids with separation of nickel cyanide.

NICKEL AND SULPHUR.

419 *Nickel Monosulphide*, NiS, occurs as millerite, being occasionally found in brass-yellow rhombohedrons, but more commonly in capillary crystals. When nickel and sulphur are heated together above the melting-point of the latter, this same compound is formed with incandescence as a bronze-yellow brittle mass which is not soluble in hydrochloric or sulphuric acid, but dissolves in nitric acid and aqua-regia. The hydrated sulphide is precipitated when ammonium sulphide is added to a nickel salt. This is difficultly soluble in hydrochloric acid, but slightly soluble with a brownish colour in ammonia, as well as in sulphide of ammonium and other alkaline sulphides, and is reprecipitated from these solutions on exposure to the air, or on addition of acetic acid. In the moist state it oxidises slowly on exposure to the air. When a solution of a nickel salt is heated with sodium thiosulphate, the monosulphide is obtained in the form of a dense black precipitate which does not undergo alteration on exposure to the air, and which is not acted upon by boiling hydrochloric acid.

Linnaeite, $(NiCoFe)_3S_4$, forms pale steel-grey crystals belonging to the regular system, and also occurs in the massive state. It is an important nickel ore occurring at various places in considerable masses, especially in the mine of La Motte in Missouri. The ore there contains, according to Genth, about 30 per cent. of nickel.

Nickel Disulphide, NiS_2, is obtained as an impalpable iron-grey powder by strongly heating a mixture of nickel carbonate, potassium carbonate, and sulphur, the residue being lixiviated with water.

NICKEL AND PHOSPHORUS.

420 Phosphorus and nickel combine when heated together to form the compound PNi_5 which also is obtained when nickel is fused together with phosphoric acid and charcoal powder. It is a silver-white, brittle, crystalline, non-magnetic mass which melts more readily than nickel. If the vapour of phosphorus be passed over red-hot nickel the compound P_2Ni_3 is obtained as a whitish-grey crystalline mass. Neither of these phosphides dissolve in hydrochloric acid, but they are readily soluble in nitric acid. If a solution of nickel chloride be added to a boiling solution of potash containing phosphorus, some tartaric acid being present in order to prevent the precipitation of the hydroxide, a black precipitate of Ni_4P_2 is thrown down. This is slowly decomposed by hydrochloric acid, and readily by nitric acid (R. Schenk).

NICKEL AND ARSENIC.

421 These two elements readily fuse together to form brittle alloys, of which some occur as minerals. Of these the most important is kupfer-nickel or nickeline, NiAs, which is found massive and also, although less frequently, crystallised in hexagonal pyramids. It has a light copper-red colour, and is an important ore of nickel, being found in various localities in Europe and America. Chloanthite, $(NiCoFe)As_2$, is another nickel arsenide occurring together with the preceding.

Detection and Estimation of Nickel.

422 Nickel is separated from other metals in the same way as cobalt. If both these metals be present, the detection as well as the separation is effected by the different reactions of their cyanides. For this purpose the sulphides are dissolved in a small quantity of aqua-regia, the solution neutralised with caustic soda, an excess of potassium cyanide added, and the

liquid boiled for a few minutes in order to form potassium cobalti-cyanide. It is then slightly acidified with hydrochloric acid. If the liquid remain clear cobalt only is present. If, on the other hand, a precipitate forms and only nickel is present, this consists of pure nickel cyanide. If both metals be present the precipitate may consist of either nickel cobalti-cyanide or of a mixture of this with nickel cyanide, according to the relative quantities of the two metals present. In the latter case nickel and cobalt are completely precipitated.

If the solution containing potassium nickel cyanide and potassium cobalti-cyanide be mixed with caustic soda and treated with chlorine in the cold, the nickel is precipitated alone as the black peroxide. This also takes place when sodium hypochlorite is added to the alkaline liquid.[1] If the solution of the cyanide be boiled with freshly precipitated mercuric oxide all the nickel is thrown down as cyanide and hydroxide. The precipitate when washed leaves after ignition pure oxide of nickel. The filtrate may be neutralised by nitric acid and mercurous nitrate added when mercurous cobalti-cyanide is precipitated, and this when ignited is converted into the oxide Co_3O_4, which may then be reduced in hydrogen and weighed as the metal.

Another separation of nickel from cobalt depends upon the precipitation of potassium cobalt nitrite (see page 134). This is dried at 100° and weighed, and the nickel in the filtrate is precipitated by caustic potash, the precipitate boiled, well washed, and converted by ignition into the monoxide.

The nickel compounds give no flame-spectrum, but the chloride yields a characteristic spark-spectrum containing a number of fine lines, of which the following are the most important:

α 5476 β 5081 γ 4715.

The spark-spectrum of the metal also contains many lines of which the brightest are:

In the orange	5892·0
In the green-blue	4872·9 4865·3 4854·7

The *atomic weight* of nickel has been often determined but not with very satisfactory results, the numbers varying between

[1] Liebig, *Ann. Chem. Pharm.* lxxxvii. 128.

58 and 59. Russell[1] in a series of well-agreeing experiments obtained the number 58·59, by reducing the strongly ignited monoxide, whilst by measuring the amount of hydrogen evolved on dissolving the pure metal he got the number 58·56.[2] On the other hand, Schneider[3] by analysing the oxalate found the numbers 57·90, and Dumas[4] by the analysis of the chloride obtained an atomic weight of 58·87.

[1] *Journ. Chem. Soc.* [2], i. 58.
[2] *Journ. Chem. Soc.* [2], vii. 292.
[3] *Pogg. Ann.* ci. 387.
[4] *Ann. Chim. Phys.* [3], lv. 129.

METALS OF THE CHROMIUM GROUP.

Chromium.	Tungsten.
Molybdenum.	Uranium.

423 The metals of this group form trioxides, which are acid-forming oxides and yield very characteristic salts. Chromium is the connecting link with the preceding group, inasmuch as its lower oxide closely resembles that of iron.

CHROMIUM, Cr = 52·4.

In 1762 Lehmann in a letter to Buffon " de nova mineræ plumbi specie crystalline rubra " described a new mineral from Siberia, now termed crocoisite or lead chromate. Vauquelin and Macquart investigated the composition of this mineral in 1789 and came to the conclusion that it contains lead, iron, alumina, and a large quantity of oxygen. However, when the former chemist re-investigated the subject in 1797, he found that the lead present was combined with a peculiar acid which he recognised as the oxide of a new metal. To this the name of *chromium* was given because all its compounds are coloured (from χρῶμα, colour). The discovery of this new metal in crocoisite was also made simultaneously and independently by Klaproth.

Chromium is not a very common substance and it does not occur in the free state. It is found in several other minerals besides crocoisite or lead chromate, $PbCrO_4$, especially as chrome-iron-stone or chromite, $FeO.Cr_2O_3$, a mineral which is the chief ore of chromium and is the one usually employed for the manufacture of the chromium compounds. Chromium also forms the colouring matter of several minerals; thus the green colour

of emerald, as was shown by Vauquelin, is due to chromium; whilst serpentine, penninite, chromic mica or fuchsite, and other minerals owe their colour to the same metal.

424 *Metallic chromium* is obtained by the reduction of the oxide or chloride. For this purpose a mixture of chromic oxide and sugar is intensely heated in a lime crucible (Deville)[1]; or chromium sesquichloride is heated with metallic zinc under a layer of sodium chloride, and the zinc-regulus treated with nitric acid, when metallic chromium remains as a grey powder (Wöhler).[2] Chromium can also be prepared by the electrolysis of a solution of chromous chloride containing chromic chloride, when the metal separates out in brittle glistening scales.[3] If chromic chloride be heated in contact with the vapour of sodium in a current of hydrogen the metal is obtained in the form of hard crystalline scales[4]; whilst when chromium amalgam is heated in an atmosphere of rock-oil the metal remains behind in the pulverulent form. The metallic regulus obtained by fusing the double chloride of chromium and potassium with zinc, leaves a residue of crystalline chromium when it is treated with nitric acid.[6]

Chromium forms a light-green glistening crystalline powder exhibiting, under the microscope, aggregations of crystals of a tin-white colour and having a specific gravity of 6·81 according to Wöhler, or of 7·3 according to Bunsen. The fused metal obtained by Deville's method is as hard as corundum, melts more difficultly than platinum, is not magnetic, and when ignited in the air or hydrogen is only slowly oxidised. Heated in the oxy-hydrogen flame it burns brightly with emission of sparks, and when fused together with saltpetre or potassium chlorate it is converted into potassium chromate. It readily combines with chlorine and dissolves quickly in hydrochloric acid. Cold dilute sulphuric acid only attacks it slowly, but, on warming, it dissolves with evolution of hydrogen. Nitric acid, even when hot and concentrated, is without action upon it (Wöhler).

Chromium Steel. The presence of from 0·5 to 0·75 per cent. of chromium in steel renders it harder than the carbon is able to do alone, and the chrome steel thus obtained is of excellent quality, but is troublesome in manipulation on account of its requiring to be worked at rather a low heat.

[1] *Comptes Rendus*, xliv. 673.
[2] *Ann. Chem. Pharm.* cxi. 230.
[3] Bunsen, *Pogg. Ann.* xci. 619.
[4] Fremy, *Compt. Rend.* xliv. 632.
[5] Vincent, *Phil. Mag.* [4], xxiv. 328.
[6] Zettnow, *Pogg. Ann.* cxliii. 477.

CHROMIUM AND OXYGEN.

425 Chromium forms two basic oxides, corresponding to those of iron, and one acid-forming oxide:

Chromium monoxide, or chromous oxide . . .	CrO.
Chromium sesquioxide, or chromic oxide . . .	Cr_2O_3.
Chromium trioxide	CrO_3.

These oxides, which are also capable of forming compounds with one another, will be described under their corresponding salts.

CHROMOUS COMPOUNDS.

426 *Chromium Monoxide*, CrO, is not known in the anhydrous state. *Chromous hydroxide*, $Cr(OH)_2$, is obtained by adding caustic potash to a solution of chromous chloride.[1] It is a brownish-yellow precipitate readily oxidised with evolution of hydrogen, and possessing a dark-brown colour when dried in absence of air. On heating, it first gives off water, and is then converted with ignition and evolution of hydrogen into the chromic oxide:

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

Chromous Chloride, $CrCl_2$, is formed when the metal is dissolved in aqueous hydrochloric acid or heated in a current of hydrochloric acid gas. It is easily obtained by the gentle ignition of the sesquichloride in a current of dry perfectly pure hydrogen. It forms white silky lustrous needles which dissolve in water with evolution of heat yielding a blue-coloured solution. This rapidly absorbs oxygen from the air and acts as a powerful reducing agent, and like solutions of the other chromous salts, rapidly absorbs nitric oxide, becoming of a brown colour.

Chromous Bromide, $CrBr_2$, is obtained by gently heating chromic bromide in hydrogen gas; it is a white crystalline mass yielding a green basic chromic bromide on exposure to the air.

Chromous Sulphate, $CrSO_4$, is only known in solution, and is prepared by dissolving the metal in dilute sulphuric acid. This

[1] Ordway *Sill. Am. Journ.* [2] xxvi. 197.

ammoniacal solution absorbs oxygen, nitric oxide, and acetylene. If potassium sulphate be dissolved in a cold saturated solution of the chloride, and then alcohol added until a precipitate begins to form, the mass being allowed to stand for some weeks in absence of air, fine blue rhombic prisms, having the composition $K_2SO_4 + CrSO_4 + 6H_2O$, are deposited, and these soon become green on exposure to the air from absorption of oxygen.

Chromous Phosphate, $Cr_3(PO_4)_2$, is a blue precipitate assuming a green colour on exposure to air.

Chromous Carbonate, $CrCO_3$, is obtained by precipitating the chloride with potassium carbonate. A yellow to greenish-blue precipitate is obtained in the cold, and this assumes a reddish-brown colour on warming.

Chromous Cyanide, $Cr(CN)_2$, is a white precipitate insoluble in potassium cyanide, changing to a dirty green on exposure to air.

Of the other chromous salts the *Acetate*, $Cr(C_2H_3O_2)_2 + H_2O$, may be mentioned. This crystallises in red rhombic prisms and absorbs oxygen so rapidly that ignition often takes place.

The chromous salts, like the ferrous salts, absorb large quantities of nitric oxide and then become brown.

CHROMIC COMPOUNDS.

427 *Chromic Oxide*, or *Chromium Sesquioxide*, Cr_2O_3, occurs in the impure state mixed with clay as chrome-ochre or wolchonskoite, and is one of the constituents of chrome-iron ore.

It is obtained artificially as a dull green amorphous powder by igniting the hydroxide, or by heating a mixture of potassium dichromate with sulphur or sal-ammoniac and lixiviating the residue. The colour of the oxide prepared by gently igniting mercurous chromate, Hg_2CrO_4, in a covered crucible is a very fine green. It melts at the temperature of the oxy-hydrogen blowpipe, solidifying to a crystalline almost black mass. Chromic oxide is also obtained in the crystalline state by fusing the amorphous substance with calcium carbonate and boron trioxide, or by ignition in a stream of oxygen. Wöhler's[1] method of preparing crystalline chromic oxide consists in passing the vapour of chromyl chloride, CrO_2Cl_2, through a red-hot tube, when chromic oxide is deposited in dark-green, lustrous, very hard,

[1] *Ann. Chem. Pharm.* lx. 203.

hexagonal crystals which have a specific gravity of 5·21. Another method consists in heating potassium dichromate either alone, or mixed with common salt; the ignited mass is dissolved in water, when chromic oxide remains in bright iridescent spangles which have a specific gravity of 5·01.[1]

The strongly ignited oxide is almost insoluble in acids, and in order to bring it into solution it must either be heated for a length of time with strong sulphuric acid or fused with acid potassium sulphate. Chromic oxide is used in the preparation of coloured glass, enamels, and porcelain, imparting to them a fine green tint. It is also used in ordinary painting, forming one of the most permanent greens, known as chrome-green.

Chromic Hydroxides. When ammonia is added to the solution of a chromic salt quite free from alkali, a pale blue precipitate is obtained, and this when dried over sulphuric acid has the composition $Cr_2(OH)_6 + 4H_2O$.[2] Three molecules of water are given off in a vacuum, and when this is heated to 200° in a current of hydrogen, the hydroxide $Cr_2O_2(OH)_2$ is formed; which begins to glow strongly at a red-heat and passes into chromic oxide. The hydroxides are soluble in acids but dissolve with difficulty.

Guignet's Green, $Cr_2O(OH)_4$, is obtained by fusing together equal molecules of bichromate of potash and crystallised boric acid, and lixiviating the fused mass with water. The residue after grinding is a fine green powder now largely used as a pigment.

Soluble Chromium Hydroxide. Freshly precipitated and washed chromium hydroxide dissolves in chromic chloride, and on dialysing this solution Graham obtained a liquid which to one molecule of hydrochloric acid contained 33 molecules of Cr_2O_3.[3] The deep dark green solution does not undergo alteration on boiling or on dilution with water, but it at once coagulates on addition of the smallest quantity of a salt.

Ammoniacal Chromic Salts. It was formerly believed that a violet modification of chromium hydroxide existed soluble in ammonia. This, however, is now ascertained to be a compound of the hydroxide with an ammonium salt possessing a constitution apparently similar to the cobaltamine salts.

If the pure hydroxide be digested for some time with concentrated ammonia a dark blue powder of $Cr_2O_2(ONH_4)_2$ is

[1] Schröder, *Pogg. Ann.* cvi. 226; cvii. 113.
[2] Ordway, *Sill. Am. Journ.* [2] xxvi. 197. [3] *Phil. Trans.* 1861, 183.

formed.[1] This dissolves in hydrochloric acid with a ruby-red colour, and from this solution *roseo-chromic chloride*, $Cr_2Cl_6(NH_3)_8 + 2H_2O$, is deposited in rhombic prisms.[2] This combines with more ammonia to form a compound soluble in water with a violet colour and precipitated by alcohol as a fine violet powder. Neither ammonia, chromium, nor chlorine can be detected in this solution by the usual reagents, but if it be boiled, chromium hydroxide separates out and then these bodies can be detected by the ordinary tests.

Chromites. Like alumina chromic oxide is a weak base though it acts towards strong bases as an acid-forming oxide. Thus a green compound of chromic oxide with an alkali is thrown down on the addition of potash or soda to a solution of a chromic salt, and the alkali cannot be removed even by boiling water. This precipitate is, however, easily soluble in an excess of the precipitant, but can be again thrown down either by partial neutralisation with acids or by boiling the solution. When caustic soda is added to a solution of a chromium salt and a salt of magnesium, a precipitate is obtained of a compound of magnesia and chromic oxide which does not dissolve in an excess of alkali.

Zinc Chromite, $ZnCr_2O_4$, is obtained by fusing the two oxides with boron trioxide at a white-heat, when blackish-green octohedrons having a specific gravity of 5·309 are obtained.

Manganese Chromite, $MnCr_2O_4$, is obtained in a similar way, and forms very hard iron-grey octohedrons, which have a specific gravity of 4·87.

Ferrous Chromite, $FeCr_2O_4$. This occurs in nature as chromite or chrome-iron-ore. It is rarely found crystallised in regular octohedrons, generally occurring massive, with a granular crystalline fracture. Alumina and magnesia occur frequently as isomorphous constituents, and in some cases chromite contains more iron than corresponds to the above formula, the composition approximating to $Fe_2Cr_2O_5 + Fe_3Cr_4O_9$.[3] Chrome-iron ore is found in the Shetland Islands, Norway, the United States, Hungary, Greece, Asia Minor, in the Urals, and in New Caledonia.

Chromoso-Chromic Oxide was obtained by Bunsen in the process of the preparation of the metal by the electrolysis of a solution of chromous chloride containing chromic chloride by

[1] Siewert *Zeitsch. ges. Naturwissensch.* xviii. 244.
[2] Cleve, *Journ. pr. Chem.* lxxxvi. 47.
[3] Christomanos, *Ber. Deutsch. Chem. Ges.* x. 343.

means of a current of low intensity. It forms a black powder insoluble in any acid, the composition of which is not constant, but varies between Cr_4O_5 and Cr_5O_6.

CHROMIC SALTS.

428 The normal chromic salts have a blue or violet colour, and allow red rays to pass through their solutions. Their cold solutions possess a violet colour, which becomes green on heating, but returns to the original colour after a time on cooling. Only the violet solutions yield crystalline salts, the green solutions depositing an amorphous green mass on evaporation. It was formerly supposed that two modifications of the chromic salts existed. According to recent investigations, however, the green solutions do not contain normal salts, but are mixtures of basic and acid ones.[1] The soluble chromic salts have an unpleasant styptic taste.

Chromic Chloride, Cr_2Cl_6, is obtained by heating an intimate mixture of chromic oxide and carbon in a stream of dry chlorine. It forms fine peach-blossom coloured scales, which have a specific gravity of 3·03, and may be sublimed at a high temperature in an atmosphere of chlorine. When heated in the air they give off chlorine, and are converted into the oxide. Chromic chloride is almost insoluble in cold water, but when treated in the finely divided state for some time with boiling water it gradually dissolves. On the other hand, it is readily soluble in presence of a very small quantity (less than 0·001 per cent.) of chromous chloride, cuprous chloride, or stannous chloride, yielding a green liquid, which may also be obtained by dissolving the hydroxide in hydrochloric acid. On slow evaporation green, freely soluble needles of $Cr_2Cl_6 + 12H_2O$ separate. These, when heated in a current of chlorine or hydrochloric acid to 250°, lose their water, leaving a residue of peach-blossom coloured scales, which are easily soluble in water, and which sublime at a high temperature, and are converted into the insoluble chloride. This is unattacked by acids, though it dissolves in alkalis after long boiling. If, however, it be placed on tinfoil, it deliquesces, undergoing a partial reduction. When the solution is evaporated

[1] Krüger, *Pogg. Ann.* lxi. 218; Loewel, *Journ. Pract. Chem.* xxxvii. 38; Siewert, *Ann. Chem. Pharm.* cxxvi. 86.

in the air, hydrochloric acid escapes, and basic chlorides of varying composition and solubility are left behind, whilst on ignition pure chromic oxide remains.

Chromic Bromide, Cr_2Br_6, is prepared in a similar way to the chloride. It forms black semi-metallic translucent hexagonal scales, having an olive-green colour, and exhibits in one direction a fine red dichroism. In its properties it closely resembles the chloride, and dissolves easily in water, when a small quantity of chromous bromide, or any other reducing agent, such as tinfoil, is present. It is obtained in solution by the action of hydrobromic acid on the hydroxide. The dark green liquid on evaporation deposits green crystals, and easily decomposes, with formation of basic salts.

No *iodide* of chromium is known.

Chromic Fluoride, Cr_2F_6, is obtained by dissolving the non-ignited oxide in hydrofluoric acid, and evaporating. It is a green crystalline mass which melts when strongly heated, and at a high temperature sublimes in regular octohedrons (Deville).

Chromic Sulphate, $Cr_2(SO_4)_3$, is obtained by mixing equal parts of concentrated sulphuric acid and chromium hydroxide dried at 100°. The mixture is allowed to stand in a loosely-stoppered bottle, when the solution, which, to begin with, is green, becomes blue, and in some weeks deposits a violet-blue crystalline mass, which is purified by solution in water and precipitation with alcohol. The violet-blue crystalline precipitate is then dissolved in weak alcohol, and this solution, after some time, deposits small regular octohedrons of $Cr_2(SO_4)_3 + 15H_2O$. When the solution of this salt is boiled or the crystals heated to 100°, a green salt is formed, which dissolves easily in alcohol, the violet salt being insoluble in this liquid. Soluble barium salts precipitate all the sulphuric acid from the violet solution in the cold, whereas the green salt is only completely precipitated after long boiling, pointing to the fact that this latter is a mixture, as has already been stated. When either the green or violet salt is heated with sulphuric acid to 190°, a pale yellow mass is obtained, which, on ignition, leaves a residue of the red anhydrous normal chromic sulphate, which is insoluble in water, and only dissolves with difficulty in acids. If dilute sulphuric acid be saturated with freshly precipitated hydroxide a green solution is obtained, and this on evaporation leaves an amorphous mass, which appears red by transmitted light, and possesses the formula $Cr_2O(SO_4)_2$. On boiling this

solution a basic salt, $2Cr_2SO_4(OH)_4 + Cr_2(OH)_6 + 5H_2O$, separates out as a pale green precipitate.

Chromic sulphate and the sulphates of the alkali metals form double salts, corresponding to the alums, to which the name of *chrome-alums* is given.

429 *Potassium Chromic Sulphate* or *Chrome-Alum*, $K_2SO_4 + Cr_2(SO_4)_3 + 24H_2O$. This substance is best obtained by the reduction of a solution of potassium dichromate, $K_2Cr_2O_7$, by adding the requisite quantity of sulphuric acid, and passing sulphur dioxide through the solution:

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

In place of sulphur dioxide any other easily oxidisable substance, such as alcohol, &c., may be employed, but in this case more sulphuric acid must be added. Chrome-alum is now obtained in large quantity as a by-product in the manufacture of artificial alizarine from anthracene, $C_{14}H_{10}$, in which the hydrocarbon is treated with a mixture of sulphuric acid and potassium dichromate when oxy-anthracene $C_{14}H_8O_2$ is formed, and this is then subjected to further treatment. The salt crystallises in large dark purple-red, almost black, octohedrons, which, when seen by transmitted light, exhibit a ruby-red colour. It dissolves in seven parts of water at the ordinary temperature. The solution has a dingy blue colour, with a tinge of red, which, when heated to 70°, becomes dark-green. After standing for several months, however, it returns to its ordinary colour. Chrome-alum is used in dyeing and calico-printing, as well as in tanning.

If chromium oxide or sulphate be fused for some hours with potassium disulphate, green microscopic needles of $Cr_2(SO_4)_3 + 3K_2SO_4$ are formed. The salt $Cr_2(SO_4)_3 + 3Na_2SO_4$ is prepared by a process similar to the corresponding potassium compound, and cannot be obtained in well developed crystals.

Ammonium Chromic Sulphate, $(NH_4)_2SO_4 + Cr_2(SO_4)_3 + 24H_2O$, is obtained by crystallising a mixture of the two salts, or by reducing the ammonium dichromate. The salt is less soluble than the potassium compound, and easily crystallises in fine ruby-red crystals, which have a specific gravity of 1·738.

Chromic Nitrate, $Cr_2(NO_3)_6 + 18H_2O$, is obtained by dissolving the hydroxide in nitric acid. The solution, which by transmitted light has a blue, and by reflected light a red colour, usually dries up to a green amorphous mass, which dissolves

only with difficulty in warm water, depositing oblique purple-red prisms.

Chromic Phosphates. The normal orthophosphate, $Cr_2(PO_4)_2$, is obtained, by the addition of phosphate of soda to a solution of chromic chloride, in the form of a green precipitate, which on drying has a dark-blue colour. If a solution of phosphate of soda be added drop by drop to one of chrome-alum, so that the whole of the chromium is not thrown down, a voluminous precipitate, which after a time becomes dark-violet and crystalline, is deposited, and has the composition $Cr_2(PO_4)_2 + 12H_2O$. If chromic hydroxide be dissolved in an excess of aqueous phosphoric acid, the solution evaporated and the residue heated to 316°, a green chromic metaphosphate, $Cr_2(PO_3)_6$, remains behind, which is insoluble both in water and in acids.

Chromic Cyanide, $Cr_2(CN)_6$, is a pale-green precipitate insoluble in potassium cyanide, which, when heated in a water bath with a solution of the latter salt in absence of air, forms

Potassium Chromicyanide, $K_6Cr_2(C_3N_3)_4$. This salt forms pale yellow monoclinic crystals, soluble in 3·24 parts of water. Its solution gives precipitates with the salts of the heavy metals, and, with sodium amalgam, it yields a red solution, inasmuch as chromous cyanide is formed, which is so readily oxidised that it has not as yet been obtained in the pure state.

430 *Chromic Thiocyanate,* $Cr_2(SCN)_6$. Chromic hydroxide dissolves in thiocyanic acid, yielding a greenish-violet solution which when concentrated over sulphuric acid dries to a dark-green amorphous deliquescent mass. It forms a series of peculiar double salts.[1]

Potassium Chromic Thiocyanate, $Cr_2(SCN)_6 + 6KSCN + 8H_2O$, is formed when a moderately concentrated solution of 6 parts of potassium thiocyanate and 5 parts of chrome-alum is heated for two hours nearly to its boiling point. On addition of alcohol to the cold solution the sulphates are thrown down and the filtrate is evaporated and crystallised from alcohol. The salt thus obtained forms quadratic almost black crystals which appear ruby-red by transmitted light and which can be obtained anhydrous at 110°. They dissolve in 0·72 parts of water, and in 0·94 parts of alcohol with a wine-red colour. On heating with alkalis they are decomposed with separation of chromic oxide, and are attacked by dilute warm hydrochloric acid.

[1] Rossler, *Ann. Chem. Pharm.* cxli. 185.

Sodium Chromic Thiocyanate, $Cr_2(SCN)_6 + 6NaSCN + 14H_2O$, possesses a light colour resembling the other chromic thiocyanates and crystallises in thin deliquescent scales.

Ammonium and barium chromic thiocyanates are also known. Lead acetate when added to a solution of the potassium salt yields a rose-red precipitate of $Cr_2(SCN)_6 + 3Pb(SCN)_2 + 4Pb(OH)_2 + 8H_2O$, and this on washing with water yields the yellow compound, $Cr_2(SCN)_6 + 2Pb(SCN)_2 + 4Pb(OH)_2 + 5H_2O$.

Silver nitrate precipitates from the solutions of the chromium thiocyanates a brown-red hydrated salt, $Cr_2(SCN)_6 + 6Ag(SCN)$, which is anhydrous at 100° and possesses a pale red colour. It is insoluble in ammonia, but soluble in potassium cyanide with a deep-red colour. If this or the lead salt be decomposed with sulphuretted hydrogen in presence of water, a dark wine-red acid solution of chromithiocyanic acid liquid is obtained, which on evaporation decomposes into chromic cyanide and thiocyanic acid.

Chromammonium Thiocyanates. When finely powdered potassium dichromate is gradually added to fused ammonium thiocyanate, ammonia is evolved and the whole of the mass becomes solid. This is then dissolved in water, the solution filtered, and a few lumps of sal-ammoniac added when scales of the salt $NH_4(SCN)_4Cr(NH_3)_2$ separate out. This salt was discovered by Morland[1] but its composition was first ascertained by Reinecke.[2] When its solution is slowly evaporated the salt crystallises in rhombic dodecahedrons having the exact appearance of small garnets; and these when warmed with caustic potash yield the potassium salt, $K(SCN)_4Cr(NH_3)_2$ is formed, which dissolves like the former salt in water with a deep red colour and crystallises in ruby red scales or cakes. Besides these, other salts of this group are known. If the rose-red insoluble mercury salt be treated with sulphuretted hydrogen the free acid, $H(SCN)_4Cr(NH_3)_2$ is obtained. This dissolves in water with a deep-red colour, and on evaporation at a low temperature is obtained as an amorphous mass. If the solution, which has a strongly acid reaction, be boiled, decomposition occurs; but a small quantity of the acid evaporates and imparts a pungent odour to the vapour.

[1] *Quart. Journ. Chem. Soc.* xiii. 252. [2] *Ann. Chem. Pharm.* cxxvi. 113.

CHROMIUM TRIOXIDE.

431 When chromic oxide is heated to redness with an alkali in presence of air or with addition of an oxidizing agent such as nitre, chlorate of potash, &c., a yellow soluble mass is obtained, consisting of an alkaline chromate. The chromates are also formed when an alkaline solution of chromic oxide is treated with lead peroxide, potassium permanganate, chlorine, bromine, hypochlorites or other oxidizing agents:

$$Cr_2O_3 + 10KOH + 3Br_2 + 2K_2CrO_4 + 6KBr + 5H_2O.$$

The chromates usually possess a yellow, yellowish-red, or red colour. Besides the normal salts we are acquainted with basic salts, but not with any acid salts. The salts usually termed acid salts are dichromates corresponding to the disulphates, and are compounds of chromium trioxide with the normal salt. Of these the most important is common red bichromate of potash, $K_2Cr_2O_7 = K_2CrO_4 + CrO_3$. We are also acquainted with trichromates and other polychromates. Chromic acid itself is only known in aqueous solution. This decomposes on evaporation yielding the trioxide.

Chromium Trioxide, CrO_3. The simplest process for preparing this compound is that described by Fritzsche.[1] For this purpose 1·5 volumes of concentrated sulphuric acid are added to one volume of a cold saturated solution of bichromate of potash. The acid is poured in a thin stream and the liquid constantly stirred. Chromium trioxide crystallises out on cooling in long needles. This method has since been modified and improved. According to Zettnow[2] the best yield is obtained when 300 grams of potassium dichromate are mixed with 500 cc. of water and 420 cc. of concentrated sulphuric acid added, and the mixture allowed to stand for twelve hours in order that the acid potassium sulphate may crystallize out. The mother-liquor is then heated to from 80° to 90°, and 150 cc. of sulphuric acid added together with enough water to dissolve the crystals of trioxide which at first separate out. After standing for twelve hours the liquid is poured off from the crystals which have separated, and a second and a third crop may be obtained by concentration. The liquid is drained

[1] *Ann. Chem. Pharm.* xxxvi. 212. [2] *Pogg. Ann.* cxliii. 471.

off from the crystals, and these are then placed on a porous plate, and washed with pure nitric acid having a specific gravity of 1·46. This is best accomplished on a filter made of pumice-stone (the trioxide being immediately reduced by organic matter) by means of a Bunsen's filter-pump, the adhering nitric acid being removed by passing a current of dry air over the crystals heated in a tube from 60° to 80°.[1]

Chromium trioxide is also easily obtained in the pure state by mixing 100 parts of barium chromate with the same quantity of water, and with 140 parts of nitric acid of specific gravity 1·38, heating the mixture to the boiling point for ten minutes, then adding 200 parts of water and again boiling the solution for some time. Barium nitrate crystallises out on cooling, and the liquid is poured off and evaporated down to the bulk of the nitric acid employed. On cooling, the liquid is again poured off from the barium nitrate and evaporated almost to dryness, a small quantity of water being added to the residue and again evaporated, and this operation continued until all nitric acid has been driven off. In this way chromium trioxide is obtained sufficiently pure for ordinary operations.[2]

Chromium trioxide exists either as a red woolly mass or as long scarlet rhombic prisms having a strong lustre, a specific gravity of 2·78, and melting at 193° to a dark-red liquid, which solidifies to a reddish-black crystalline mass having a metallic appearance. If a large amount of the fused oxide be allowed quietly to cool with a thermometer placed in it, the temperature is seen to sink to 170° before solidification begins, but, then it rises to 195°. At 250° it is resolved into oxygen and the sesquioxide.

Chromium trioxide is easily converted into chromic oxide, by reducing agents, such as sulphur dioxide, hydrogen sulphide, zinc dichloride, arsenic trioxide, zinc, &c. Many organic compounds also act in the same way. Thus if strong alcohol be dropped on to the dry trioxide reduction takes place with incandescence, and, if the trioxide be previously mixed with a little powdered camphor, the chromic oxide formed assumes the appearance of a green mossy vegetation. Paper, sugar, oxalic acid, &c., also reduce the solution of the trioxide especially on warming. When the trioxide is heated with hydrochloric acid chlorine is liberated, and when heated with sulphuric acid it

[1] Bunsen, *Ann. Chem. Pharm.* cxlviii. 290.
[2] Duvillier, *Compt. Rend.* lxv. 711.

decomposes with evolution of oxygen. The aqueous solution of chromium trioxide as well as its solution in glacial acetic acid is often used in organic chemistry as an oxidising agent. Still more commonly a mixture of potassium dichromate and dilute sulphuric acid is employed for this purpose, in which case, as has already been stated, chrome-alum is obtained as a by-product. Chromium trioxide dissolves without alteration in cold dilute alcohol and in pure ether, and it is also soluble in concentrated sulphuric acid, but not in an acid containing from 16 to 17 per cent. of water. It deliquesces on exposure to air, forming a brown solution which on dilution with water becomes of a yellowish-red colour. This dyes the skin as well as silk and wool of a yellow colour, and possesses an acid and astringent taste.

THE CHROMATES.

432 *Normal Potassium Chromate*, or *Yellow Chromate of Potash*, K_2CrO_4, is obtained by the addition of potash to a solution of the bichromate. On evaporating the solution yellow rhombic pyramids crystallise out, which are isomorphous with potassium sulphate, and crystallise with the latter salt in all proportions. It has a specific gravity of 2·71 at 3°·9, and it does not undergo alteration in the air. On heating, it becomes red-coloured and melts at a high temperature without decomposition, solidifying on cooling to a crystalline mass. It dissolves in water with a yellow colour which is perceptible even when very small quantities of the substance are present, one part of the salt imparting a distinct yellow tint to 400,000 parts of water. One hundred parts of water dissolve:

At	0°	20°	60°	100°
K_2CrO_4	58·90	62·94	71·02	79·10 parts.

The saturated solution boils at 104°·2. The salt has a bitter cooling taste and an alkaline reaction. On evaporating its solution red crystals of the dichromate are first deposited and afterwards the yellow crystals of the neutral salt. It is decomposed by all acids, even by carbonic acid with formation of the dichromate. It is insoluble in alcohol.

433 *Potassium Dichromate*, or *Bichromate of Potash*, $K_2Cr_2O_7$, serves as the point of departure for the preparation of almost all

the other chromium compounds, and is prepared on the large scale from chrome-iron ore.

Up to the year 1820, potassium dichromate was used only for the purpose of making chrome-yellow, and was prepared by the calcination of chrome-iron-ore with costly saltpetre. In the above year Köchlin introduced potassium dichromate into the process of Turkey-red dyeing, and it soon was employed for a variety of other purposes, especially in wool-dyeing. In its preparation potashes were employed instead of saltpetre, and the chrome-iron-stone was oxidised in reverberatory furnaces by means of atmospheric oxygen. An important improvement was made in the process by Stromeyer by the introduction of a certain quantity of lime together with the potash. Not only was a saving of alkali thus effected, but the oxidation was rendered easier, inasmuch as the whole mass did not fuse, and therefore remained porous and more capable of absorbing the atmospheric oxygen. The chrome-iron-ore is first roasted and $4\frac{1}{2}$ parts of the finely ground ore mixed with $2\frac{1}{4}$ parts of potassium carbonate and 7 parts of lime. This mass after drying at 150° is heated to bright redness with an oxidizing flame, the whole being constantly stirred. At the end of the operation the charge is withdrawn from the furnace and after cooling it is lixiviated with the minimum amount of hot water. If calcium chromate be found in solution a hot saturated solution of potassium sulphate is added, when the lime is thrown down as sulphate and potassium chromate remains in solution. The liquor is next treated with the requisite quantity of sulphuric acid, diluted with twice its volume of water, to convert the chromate into dichromate, and then allowed to cool. The solution of chromate saturated at 16° contains nearly 1 part of salt to 2 parts of water, whilst the dichromate requires 10 parts of water for its solution. It is clear, therefore, that when the saturated solution of chromate is converted into dichromate, a precipitate of about three-quarters of the dichromate will be formed on cooling. This precipitate is collected and then recrystallized. The mother-liquor, which of course contains potassium sulphate, is used for the lixiviation of another portion of the roasted mass.

Potassium dichromate crystallises in splendid garnet-red tables or prisms belonging to the triclinic system, having a specific gravity of 2·692 at 3°·9. It melts below a red-heat forming a transparent red liquid, which when slowly cooled solidifies

in crystals which have the same form as those deposited from aqueous solution. It decomposes at a white-heat into oxygen, chromic oxide, and the normal salt. One hundred parts of water dissolve :

At	0°	10°	40°	80°	100°
$K_2Cr_2O_7$	4·96	8·47	29·15	73·00	102·04.

The saturated solution boils at 104°. Potassium dichromate has an acid reaction, a cooling bitter metallic taste, and is insoluble in alcohol; it acts as a powerful poison, probably on account of its oxidizing properties. The commercial salt is usually almost chemically pure, and is employed for the preparation of the other chromium compounds, as a reagent, and as an oxidizing agent, as well as being largely used in dyeing and calico-printing.

A film of organic matter saturated with a solution of potassium dichromate acquires a dark colour on exposure to light owing to a reduction to chromic oxide taking place, and a solution of this substance in gelatine is used as a sensitive agent in the Autotype and other similar *photographic printing* processes. These processes depend not merely upon the de-oxidation of the dichromate, but also upon the fact that this reduction renders the gelatine insoluble in and non-absorbent of water, so that those portions of the gelatine-film which have been acted upon by the light remain unchanged when the film is immersed in hot water, while those parts which have been protected from the action of the light, dissolve away entirely. A film is thus obtained in which the various shades of the original negative are represented by deposits of varying thickness, of the insoluble gelatine, which can be coloured with any desired pigment, and in this way the red- or blue-chalk drawings of the old masters can be produced in exact fac-simile.[1]

Potassium dichromate forms a double salt with mercuric chloride, $K_2Cr_2O_7 + HgCl_2$, which separates out in red rhombic crystals. When potassium dichromate is dissolved in 12 parts of hot nitric acid, carmine-coloured tables of potassium nitro-dichromate, $KCr_2O_6NO_2$, are formed. These when crystallised from nitric acid yield garnet-red crystalline scales of potassium nitro-trichromate, $KCr_3O_9NO_2$.

Potassium Trichromate, $K_2Cr_3O_{10}$, crystallises in dark red

[1] For a full and interesting description of these processes, see Abney's *Treatise on Photography*. Longmans : 1878, pp. 32, 160.

nacreous prisms when a solution of the dichromate in ordinary nitric acid, or in an aqueous solution of chromium trioxide, prepared at 60°, is allowed to cool. These have a specific gravity of 3·613, melt at a temperature of 150°, and gradually become black on exposure to air (Graham).

Potassium Tetrachromate, $K_2Cr_4O_{13}$, is obtained in the form of thin glistening red scales, when the foregoing salt is heated for some time with concentrated sulphuric acid.

Normal Sodium Chromate, $Na_2CrO_4 + 10H_2O$. This is obtained by fusing chromic oxide and sodium nitrate together, and evaporating the solution at a low temperature, or by allowing a solution of chromate of potash saturated with soda to evaporate at 0°. The salt is deposited in deliquescent transparent yellow prisms, isomorphous with glauber salt. Heated to above 30° the anhydrous salt separates out. It has an alkaline reaction, and a bitter metallic taste.

Sodium Dichromate, $Na_2Cr_2O_7 + 2H_2O$, crystallises in thin yellowish-red deliquescent prisms.

434 *Normal Ammonium Chromate*, $(NH_4)_2CrO_4$, is obtained by evaporating a solution of the trioxide with excess of ammonia at temperatures below 60°, when lemon-yellow needles separate which are permanent in the air, easily soluble in water, possess an alkaline reaction, and leave chromic oxide when ignited.

Ammonium Dichromate, $(NH_4)_2Cr_2O_7$, is formed when the requisite quantity of the trioxide is added to ammonia. On evaporation, orange-coloured monoclinic crystals having a specific gravity of 2·367 separate out. They are permanent in the air, and when ignited decompose into nitrogen, water, and flocculent chromic oxide, which swells up to a large bulk.

If solutions of equal parts of ammonium dichromate and mercuric chloride are evaporated, large red six-sided monoclinic prisms, having the formula $(NH_4)_2Cr_2O_7 + HgCl_2 + H_2O$, are deposited; whilst from the mother-liquor another salt, $3(NH_4)_2Cr_2O_7 + HgCl_2$, crystallises in needles.

Ammonium Trichromate $(NH_4)_2Cr_3O_{10}$, and *Ammonium Hexchromate* $(NH_4)_2Cr_6O_{19}$, are also known.

Barium Chromate, $BaCrO_4$, is an insoluble yellow precipitate, having a specific gravity of 3·9. It is insoluble in acetic, but easily soluble in nitric, hydrochloric, and aqueous chromic acids. From the last solvent the salt $BaCr_2O_7 + 2H_2O$ may be obtained in yellow stellar needles, which are decomposed by water with

separation of the normal salt. Barium chromate is used as a pigment under the name of yellow ultramarine.

Magnesium Chromate, $MgCrO_4 + 7H_2O$, crystallizes from a solution of magnesia in chromic acid in lemon-yellow crystals isomorphous with sulphate of magnesia. Its specific gravity is 1·66.

Magnesium Potassium Chromate, $MgCrO_4 + K_2CrO_4 + 2H_2O$, crystallizes in yellow four-sided tables on evaporating a solution of potassium dichromate which has been neutralised with magnesia.

Magnesium Ammonium Chromate, $MgCrO_4 + (NH_4)_2CrO_4 + 6H_2O$, is isomorphous with the corresponding sulphate.

Zinc Chromates. Chromate of potash gives with zinc sulphate a yellow precipitate of basic zinc chromate, $Zn_2(OH)_2CrO_4 + H_2O$. A similar compound, $2Zn_2(OH)_2CrO_4 + H_2O$, is formed when zinc carbonate is heated with a solution of chromic acid.

If zinc oxide or a zinc salt is boiled with potassium dichromate the yellow insoluble compound, $Zn_4(OH)_6CrO_4$, is precipitated.

435 *Lead Chromate*, $PbCrO_4$, occurs as crocoisite in translucent yellow monoclinic prisms, having a specific gravity of 5·9 to 6·1. The mineral is found in Siberia, in the Urals, Brazil, Hungary, and the Phillippine islands. Crystals having a specific gravity of 6·118 are artificially obtained when lead chloride is strongly heated with potassium chromate, as well as when solutions of lead acetate and normal potassium chromate are allowed slowly to diffuse into one another.[1] A bright yellow precipitate of the normal chromate is obtained when a solution of a lead salt is precipitated with potassium dichromate. This goes under the name of *chrome-yellow*, and is largely used as a pigment. It is insoluble in water, but readily dissolves in nitric acid and caustic potash. When strongly heated it fuses to a brown liquid, which on cooling solidifies to a crystalline mass. As lead chromate at a red-heat oxidises all organic substances, it is frequently employed in organic analysis, especially in the case of bodies which contain chlorine, sulphur, &c. The chrome-yellow of commerce often contains admixtures, especially lead sulphate. This, however, is not always to be considered as an adulteration, as it is used for the preparation of a light shade. This is termed Cologne-yellow, and is obtained by a precipitation of the mixture of the nitrates of lead and calcium with a mixture of sodium

[1] Drevermann, *Ann. Chem. Pharm.* lxxxvii. 121.

sulphate and potassium chromate, or more generally by heating lead sulphate with a solution of potassium dichromate.

Calico is printed or dyed with chrome-yellow, by first mordanting the cloth with a solution of lead salt, and afterwards steeping it in one of chromate of potassium.

Basic Lead Chromate, Pb_2CrO_5, occurs in commerce as *chrome-red*, and is obtained as a fine red powder by digesting chrome-yellow with cold caustic soda, or boiling it with a solution of normal potassium chromate, or by fusing it with nitre. The *chrome-orange* of commerce is a mixture of chrome-red and chrome-yellow obtained by treating the latter with milk of lime or by precipitating a lead solution with a weak alkaline solution of potassium chromate. Another basic salt, $Pb_3Cr_2O_9$, occurs as the mineral phœnicite in hyacinth-red crystals, having a specific gravity of 5·75. It may be artificially prepared together with the normal chromate, by allowing solutions of lead nitrate and potassium chromate to diffuse into one another when it separates in dark-red tables.

436 *Copper Chromates.* *Copper dichromate*, $CuCr_2O_7+2H_2O$, is obtained by the action of concentrated chromic acid solution on copper hydroxide. It forms blackish-brown deliquescent crystals. The solution when boiled deposits the basic salt $Cu_3CrO_6 + 2H_2O$ as a brown precipitate, which is also obtained when boiling solutions of normal potassium chromate and copper sulphate are mixed. Cold solutions, on the other hand, yield the double salt $K_2CrO_4 + Cu_3Cr_2O_9 + 2H_2O$, which is obtained also by the action of potassium dichromate solution on freshly precipitated copper hydroxide in pale brown microscopic six-sided tables. The mineral vauquelinite, $(CuPb)_3Cr_2O_9$, occurs in small glistening monoclinic crystals or earthy masses, together with crocoisite.

Normal Silver Chromate, Ag_2CrO_4, is obtained as a red crystalline precipitate when a dilute solution of potassium chromate is poured into a concentrated solution of silver nitrate. If silver oxide be boiled for some time with a solution of potassium dichromate, the same compound is obtained as a cherry-red powder consisting of needle-shaped crystals. It is insoluble in water, but soluble in nitric acid, ammonia, and the chromates of the alkali metals. On evaporation, it separates from the ammoniacal solution as a green metallic glistening crust, which yields a red powder.

Silver Dichromate, $Ag_2Cr_2O_7$, is formed when a solution of

potassium dichromate is dropped into concentrated silver solution. The scarlet precipitate is slightly soluble in water, and crystallises in red triclinic crystals, which are decomposed by boiling water.

Ammonio-Silver Chromate, $Ag_2CrO_4 + 4NH_3$, is obtained by dissolving the normal salt in ammonia, and evaporating the solution, when it deposits in yellow transparent crystals, which are isomorphous with the corresponding sulphate, and lose ammonia on exposure to air.

Mercurous Chromate, Hg_2CrO_4, is a bright red crystalline precipitate, obtained by adding potassium dichromate to an excess of mercurous nitrate. On heating it decomposes with evolution of mercury and oxygen, bright green chromic oxide remaining behind.

Mercuric Chromate, $HgCrO_4$, is formed when equal parts of chromium trioxide and mercuric oxide are boiled together with water. It crystallises in garnet-red rhombic prisms, which are decomposed by water, especially when warm, with formation of the amorphous insoluble basic salt, Hg_3CrO_6. If freshly precipitated mercuric sulphide be warmed for some hours with solution of chromium trioxide, and the product dried at the ordinary temperature, a yellow-ochre coloured powder is obtained, which has the composition $2HgCrO_4 + HgS$, which, on percussion or heating, explodes very violently.

Ferric Chromate, $Fe_2(CrO_4)_3$, is obtained as a bright yellow powder, by precipitating a neutral ferric chloride solution with a hot saturated solution of potassium dichromate. If ferric hydroxide be digested with a solution of chromium trioxide and evaporated, a brown mass having the composition $Fe_2Cr_4O_{15}$ is obtained, which is soluble in water and alcohol.

437 *Chromic Chromate*, $Cr_2O_3 . CrO_3 = 3CrO_2$. This compound, also known as chromium dioxide or peroxide, is formed when chromic nitrate is gently heated. It is likewise prepared by the partial reduction of the trioxide, and by the precipitation of chromic salt with a soluble chromate. The brown powder thus obtained is easily soluble in acids. Alkalis precipitate chromic hydroxide from its solution, whilst a chromate remains in the liquid. If chromium chromate be washed for some time with water, it is decomposed into soluble trioxide and insoluble sesquioxide. When nitric oxide is passed into a tolerably concentrated solution of bichromate of potash, chromic chromate is obtained as a dark-brown precipitate, which dries at 250° to form

a black hygroscopic powder, and this, when heated in a current of hydrochloric acid, yields chromic oxide, water, and chlorine.

When vapour of chromic chloride is passed through a red-hot tube, violet translucent prisms, having the composition $Cr_5O_9 = 2Cr_2O_3 + CrO_3$, are obtained. These are magnetic, and on ignition are gradually converted into chromic oxide.[1]

CHROMYL CHLORIDE AND THE CHLOROCHROMATES.

438 *Chromium Oxychloride or Chromyl Chloride,* CrO_2Cl_2. *Vapour Density* = 77·5. This compound, sometimes termed chlorochromic acid, appears to have been discovered by Thompson,[2] and was afterwards specially investigated by Berzelius and Wöhler.[3] It is prepared by distilling a fused mixture of ten parts of common salt and twelve parts of bichromate of potash, together with thirty parts of concentrated sulphuric acid, and in order to remove free chlorine repeatedly rectifying the distillate in a current of carbon dioxide. It is a mobile liquid of a splendid blood-red colour by transmitted, and nearly black as seen by reflected light. It boils at 118°, and has a specific gravity at 25° of 1·920.[4] It absorbs chlorine readily, dissolves iodine, and when dropped into water it remains unaltered for a few seconds, but is afterwards decomposed with violent ebullition into chromic and hydrochloric acids. The specific gravity of the vapour of chromyl dichloride is, according to Bineau, 5·39 (air = 1). When brought into contact with phosphorus it explodes, whilst it takes fire in contact with sulphur, hydrogen sulphide, ammonia, alcohol, and many other organic bodies, and when diluted with acetic acid, acts as an oxidizing and chlorinating agent upon hydrocarbons. When heated in a closed tube to 180° for three or four hours *trichromyl chloride,* $Cr_3O_6Cl_2$, is formed as a black powder, which deliquesces on exposure to the air.[5]

Chloro-chromates. Chloro-chromic acid, $HCrO_3Cl$, standing between chromic acid and its chloride, and corresponding to chloro-sulphonic acid (Vol. I. p. 345) has, like chromic acid itself, not been obtained in the pure state. The salts, however, of this acid are known.

[1] Geuther, *Ann. Chem. Pharm.* cxviii. 61. [2] *Phil. Trans.* 1827, p. 159.
[3] *Pogg. Ann.* xxxiii. 343. [4] Thorpe, *Chem. Soc. Journ.* xxi. 514.
[5] *Ibid,* xxiii. 31.

Potassium Chloro-chromate, $KCrO_3Cl$, was discovered by Péligot,[1] and is formed when three parts of potassium dichromate are gently heated with four parts of concentrated hydrochloric acid and a small quantity of water. Also by adding chromyl chloride to a saturated solution of potassium chloride:

$$CrO_2Cl_2 + KCl + H_2O = KCrO_3Cl + 2HCl.$$

This crystallizes in flat red rectangular prisms, having a specific gravity of 2·497. The salt is partially decomposed by water, but may be re-crystallized from water containing hydrochloric acid. It decomposes at 100°, with evolution of chlorine. Dry ammonia converts it into a mixture of sal-ammoniac, potassium chloride, and the salt $K_2Cr_3O_8$, crystallizing in brown-red hexagonal scales. If ammonia be passed into ether containing the salt in suspension, potassium amido-chromate, $KCrO_3NH_2$, crystallizes out in garnet-red prisms. This is decomposed by nitrogen trioxide in aqueous solution, with formation of nitrogen, water, and potassium dichromate:

$$2KCrO_3NH_2 + N_2O_3 = 2N_2 + 2H_2O + K_2Cr_2O_7.$$

Chloro-chromates of sodium, ammonium, calcium, and magnesium have also been described by Péligot.

439 *Chromium Hexfluoride*, CrF_6. This compound, corresponding to the trioxide, was discovered by Unverdorben,[2] and is obtained by heating a mixture of four parts of ignited chromate of lead, three parts of pure fluor-spar, and five parts of fuming sulphuric acid in a lead or platinum vessel. It is a red gas, which condenses to a blood-red strongly fuming liquid. The vapour, when inhaled, produces violent coughing and severe oppression of the lungs. It is decomposed by water, with formation of hydrofluoric acid and chromium trioxide. This latter is obtained in the pure state by passing the vapours into a platinum crucible, covered with a wet piece of filter-paper, when the trioxide separates as a red woolly mass.

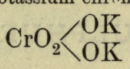
Potassium Fluo-chromate, $KCrO_3F$, is formed when bichromate of potash is heated with concentrated hydrofluoric acid in a platinum vessel. It crystallizes in red quadratic pyramids which are decomposed by hot water into potassium dichromate and hydrofluoric acid.

[1] *Journ. Pharm.* June 1833.
[2] *Trommsd. N. Journ. Pharm.* ix. 22.

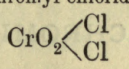
The Constitution of the Chromates, Chloro-chromates, and similar compounds.

440 The chromates and their derivatives may be considered to contain the radical chromyl, CrO_2, in the same way that the existence of the diad radical sulphuryl, SO_2, is assumed in sulphuric acid and the compounds derived from it. The constitution of the above compounds may be gathered from the following formulæ:

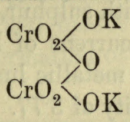
Potassium chromate.



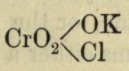
Chromyl chloride.



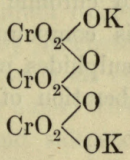
Potassium dichromate.



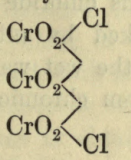
Potassium chloro-chromate.



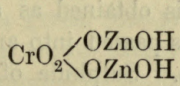
Potassium trichromate.



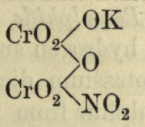
Trichromyl chloride.



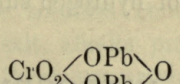
Basic zinc chromate.



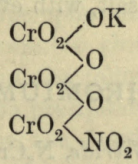
Potassium nitro-dichromate.



Basic lead chromate.



Potassium nitro-trichromate.



Perchromic Acid, $HCrO_4$. A deep indigo-blue coloured solution is obtained when hydrogen dioxide is added to an aqueous solution of chromium trioxide, or to a solution of a chromate acidified with sulphuric acid. This blue liquid, which probably

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consists of perchromic acid, quickly decomposes, with evolution of oxygen. If the freshly-prepared solution be shaken with ether, this liquid takes up the perchromic acid, and becomes of a dark-blue colour. The ethereal is more stable than the aqueous solution, but on evaporation it leaves a residue of chromium trioxide. The same decomposition is effected by alkalis, a chromate being formed with evolution of oxygen. The colouring power of perchromic acid is so great that its formation is employed as the most delicate test, both for chromic acid and for hydrogen dioxide.

CHROMIUM AND SULPHUR.

441 *Chromium Sesquisulphide, or Chromium Sulphide*, Cr_2S_3. This is obtained by heating chromium with sulphur, or by igniting chromic chloride, or the trioxide, in a current of hydrogen sulphide. It forms either a blackish-grey metallic lustrous powder, or an elastic mass having a specific gravity of 3·77. When heated in the air it burns with formation of the green oxide, and in chlorine yields chloride of sulphur and chromic chloride. It is not attacked by nitric acid. This compound cannot be prepared in the wet way, as soluble sulphides precipitate the hydroxide from chromic salts, with liberation of sulphuretted hydrogen:

$$Cr_2Cl_6 + 6H_2O + 3(NH_4)_2S = Cr_2(OH)_6 + 6NH_4Cl + 3H_2S.$$

Chromium Persulphide, Cr_2S_7, is obtained as a brown precipitate when hydrogen sulphide is passed into an ammoniacal solution of potassium dichromate. Sulphide of carbon does not extract sulphur from the compound. It is slowly decomposed by water, and dilute acids decompose it into free sulphur and a chromic salt, with evolution of hydrogen sulphide.

CHROMIUM AND NITROGEN.

Chromium Nitride, N_2Cr_2, is formed by the direct union of its elements at a red-heat[1]; and also by passing ammonia over heated chromic chloride. It is a brownish-black powder, which takes fire and burns when heated to 200° in the air or in oxygen. Cold

[1] Briegleb and Geuther, *Ann. Chem. Pharm.* cxxiii. 239.

chlorine does not act upon it, but when heated in this gas small explosions first occur, owing to formation of nitrogen chloride, and at last chromic chloride remains. It does not undergo change on ignition in hydrogen or in aqueous vapour, and is not attacked by caustic potash, hydrochloric acid, or nitric acid. Concentrated sulphuric acid converts it into ammonia chrome-alum:

$$Cr_2N_2 + 4H_2SO_4 = Cr_2(SO_4)_3 + (NH_4)_2SO_4.$$

CHROMIUM AND PHOSPHORUS.

Chromium Phosphide, P_2Cr_2, is obtained by passing the vapour of phosphorus over ignited chromate of potash. On lixiviating the black fused mass with water, a crystalline powder remains behind, having a metallic lustre, and possessing the above composition. When heated in oxygen this powder takes fire, and burns with formation of chromic phosphate.

Detection and Estimation of Chromium.

442 Chromium oxide is frequently detected in its insoluble compounds by its characteristic green colour, as well as by the fact that it forms an emerald-green bead, both in the oxidizing and reducing flame, with borax or microcosmic salt. On fusion with soda and saltpetre a yellow mass is obtained, which is soluble in water, and the solution acidified by acetic acid yields a yellow precipitate with soluble lead salts. Caustic potash or soda gives a green precipitate in solutions of chromic salts. This dissolves in an excess of alkali in the cold, but is completely precipitated on boiling the solution. This reaction is employed for the separation of chromium from aluminium, metals which are obtained together in the course of analysis. If, however, the solution contains large quantities of a zinc or magnesium salt, alkalis produce insoluble chromates of these metals, and these are precipitated in the following operations, together with iron. In this case the precipitate must be fused with saltpetre and carbonate of soda, the fused mass dissolved in water, and the filtrate tested for a chromate. The detection of chromic acid is rendered easy by the bright yellow or red colour of its salts. The yellow colour of the normal chromates becomes red on the addition of an acid, and again yellow when

made alkaline. Silver nitrate precipitates the normal chromates of a purple-red, and the dichromates of a dark-red colour, both precipitates being easily soluble in ammonia and in dilute nitric acid. Barium chloride gives a pale yellow precipitate, with solutions of the normal chromates, and lead acetate throws down a pale yellow powder, insoluble in nitric acid, turned red by a slight excess of caustic potash, and soluble in a large excess of this reagent, and from this solution acetic acid again precipitates chrome-yellow. All the chromates are converted by reducing agents into the chromic salts. When they are distilled in the dry state with common salt and sulphuric acid, they yield red vapours of chromyl chloride, which condense to a dark-red liquid, becoming yellow on saturation with ammonia.

The chromium salts do not impart any colour to the non-luminous gas-flame. The solution of chromic chloride gives a spark-spectrum containing lines of which the two following are the most characteristic:

$$\alpha\ 5205 \qquad \beta\ 4255.$$

The spark-spectrum of the metal is a complicated one. The following are the brightest lines:

In the green . . .	5207·6 5205·2 5205·7	In the dark blue .	4289·4 4274·6 4253·9

In order to determine chromium *quantitatively* in the chromium salts, a hot solution is precipitated with an excess of ammonia, the solution heated nearly to the boiling point, and the precipitate well washed with hot water, dried, ignited, and weighed as chromic oxide. In the chromates the chromium is either determined by precipitation in acetic acid solution with lead acetate, and weighing the precipitated lead chromate ignited at a dull red-heat, or the solution is mixed with hydrochloric acid and alcohol, in order to form chromic chloride, which is then determined as above. Another good method is to precipitate the neutral solution, or one made slightly acid by nitric acid, with mercurous nitrate, and to convert the washed and dried precipitate by ignition into chromic oxide.

For the valuation of Chrome Iron Ore the following process may be adopted. Eight parts of borax are fused in a platinum crucible, one part of the finely pulverized ore added, and the crucible kept at a bright red-heat for half an hour. Dry car-

bonate of soda is next added as long as effervescence ensues, and then three parts of a mixture of equal weights of carbonate of soda and nitre are gradually introduced, the mass being frequently stirred with a platinum wire. The alkaline chromate is dissolved in water, and to get rid of the silica and alumina which are in solution, it is evaporated nearly to dryness on a water-bath with an excess of ammonium nitrate, until all free ammonia is expelled. Water is now added, the liquid filtered, and the chromium in solution estimated as above described.

Another convenient method consists in igniting 0·5 gram of the finely powdered mineral with 10 grams of caustic soda and 15 grams of magnesia for one hour over a Bunsen burner, stirring the powder with a platinum wire. After fusion the mass is treated with water, the filtrate acidified with hydrochloric acid, and the chromium determined volumetrically with ammonium ferrous sulphate.[1]

The atomic weight of chromium has not been determined with a great degree of accuracy. The numbers obtained by different experimenters, especially the older ones, vary considerably, chiefly owing to the inexactitude of the methods employed. The careful analysis made by Berlin[2] of the silver salt gave numbers varying from 52·4 to 52·5. Kessler[3] determined the equivalent quantities of potassium dichromate and potassium chlorate needed to oxidize a given quantity of arsenic trioxide to pentoxide, obtaining the number 52·2; and lastly, Siewert,[4] from an analysis of the violet chloride, found the atomic weight to be 52·0.

MOLYBDENUM, Mo = 95·8.

443 The name *Molybdæna*, which occurs in the writings of Dioscorides and Pliny, is derived from the Greek word μόλυβδος, lead, and was originally employed for the designation of a variety of substances containing lead. At a later time the name was used to signify galena or substances similar in appearance to this body, and to these bodies the name of plumbago or black-lead was also given. Even sulphide of antimony and pyrolusite, to which latter mineral Linnæus gave

[1] Christomanos, *Ber. Deutsch Chem. Ges.*, x. 16.
[2] *Ann. Chem. Pharm.* lvi. 207; lx. 182.
[3] *Pogg. Ann.* cxiii. 137.
[4] *Zeitschr. Ges. Naturwis.* xvii. 530.

the name of molybdænum magnesii, were also classed under the same group of bodies. At a still later period this word was entirely applied to graphite and to the mineral sulphide of molybdenum, which is extremely similar in its appearance to graphite.

The difference between plumbago and the sulphide of molybdenum was first pointed out by Scheele in his treatise on "Molybdæna" in 1778, and another on "Plumbago" in 1779.[1] By heating the former mineral with nitric acid he obtained sulphuric acid together with a peculiar white earth which he recognised as an acid-forming oxide, and termed it *acidum molybdænæ*, and he assumed that the mineral is a compound of this acid with sulphur. In 1781 Bergman suggested that the earth was probably a calx of a metal, and in 1782 he wrote that Hjelm had succeeded in preparing the metal, though the details of the experiments were first made known in 1790.

Another mineral containing molybdenum is the yellow molybdate of lead or wulfenite first found in Carinthia. This was investigated by the elder Jacquin, and he showed that it contained lead, but was doubtful as to the nature of the acid with which this metal is combined. Salzwedel, who analyzed it in 1790, believed that it was a lead salt of tungstic acid, but Klaproth in 1797 ascertained its true composition. The compounds of molybdenum were then more accurately examined by Berzelius.

Molybdenum is usually found as molybdenite, MoS_2; also as wulfenite, $PbMoO_4$; more rarely it occurs as molybdic ochre, MoO_3, and pateraite, $CoMoO_4$. Iron ores frequently contain traces of molybdenum, and hence this metal is also found in pig-iron as well as in the slag. Thus the iron-slag obtained in the process of melting the cuprous schist at Mansfeld, is said to contain from 9 to 28 per cent. of molybdenum.[2]

Preparation of Metallic Molybdenum. In order to prepare the metal, the trioxide or one of the chlorides is heated to redness in a current of hydrogen.[3] The reduction of the trioxide does not take place readily, and for this reason the product is heated at the end of the operation in a current of dry hydrochloric acid, when any of the unreduced trioxide is converted into the volatile compound, $MoO_3Cl_2H_2$.[4]

[1] *Vetensk. Acad. Handl.* [2] Heine, *Journ. Pract. Chem.*, ix. 177.
[3] Wöhler, *Ann. Chem. Pharm.* xciv. 255.
[4] Liechti and Kempe, *Ann. Chem. Pharm.* clxix. 344.

Pure molybdenum has a silver-white colour, is harder than silver, has a specific gravity of 8·6,[1] and does not fuse completely at the highest temperature of a wind-furnace (Bucholz); indeed according to Debray it is infusible at that temperature. When one of the oxides is ignited in a carbon crucible the resulting molybdenum contains from 4 to 5 per cent. of carbon, and this product can be fused in the oxy-hydrogen blowpipe. Molybdenum is oxidized only when heated in contact with the air. It decomposes water at a red-heat, and it is readily soluble in nitric acid and hot concentrated sulphuric acid as well as in aqua regia. It is not attacked by hydrofluoric acid or by dilute sulphuric or hydrochloric acids.

OXIDES AND CHLORIDES OF MOLYBDENUM.

444 Molybdenum is remarkable for the number of oxides and corresponding chlorides which it forms, the following being known:

OXIDES.		CHLORIDES.	
Molybdenum Monoxide,	Mo O.	Molybdenum Dichloride,	$Mo Cl_2$.
,, Sesquioxide,	Mo_2O_3	,, Sesquichloride,	Mo_2Cl_6.
,, Dioxide,	$Mo O_2$.	,, Tetrachloride,	$Mo Cl_4$.
		,, Pentachloride,	$Mo Cl_5$.
,, Trioxide,	$Mo O_3$.		

It will be convenient to class the several corresponding compounds together, and to describe them in the above order.

The three first oxides are basic, but only the chlorides and bromides have been satisfactorily examined. The trioxide, the most important oxide, is an acid-forming oxide like the corresponding chromium compound.

445 *Molybdenum Monoxide*, MoO, is obtained in the hydrated state as a black powder by the action of hot potash on the corresponding chloride or bromide.

Molybdenum Dichloride, $MoCl_2$, is prepared by heating the sesquichloride in a current of dry carbon dioxide:

$$Mo_2Cl_6 = MoCl_2 + MoCl_4.$$

The tetrachloride volatilizes, and the dichloride remains as a sulphur-yellow amorphous powder, which does not alter in contact with the air, does not dissolve in water, and is soluble in alcohol and ether, separating from these solutions in the amorphous

[1] Debray, *Compt. Rend.* xlvi. 1098.

condition.[1] It is also soluble in the hydracids and in hot sulphuric acid, and in the alkalis, from which latter solution the monoxide separates on boiling. The hydrate, $MoCl_2 + H_2O$, crystallizes from the hydrochloric acid solution on standing in pale-yellow plates insoluble in water, but when the solution is evaporated long prisms having the formula, $MoCl + 2H_2O$, are deposited. These are soluble in water and when dissolved in hot hydrochloric acid long glittering needles of the compound, $MoCl_2 + 3H_2O$, are deposited. These do not dissolve in water, but are decomposed by it with evolution of hydrochloric acid.

Molybdenum Dibromide, $MoBr_2$, is formed by the decomposition of the tribromide by heat. It forms a yellowish-red infusible mass which does not dissolve in water or in acids.

The molecular formulæ of these two compounds are probably treble of those which are here given, for if the chloride be dissolved in caustic potash the compound, $Mo_3Cl_4(OH)_2 + 2H_2O$, is thrown down on the addition of acetic acid in the form of a pale yellow amorphous precipitate. This compound, which has been termed *chloro-molybdic hydroxide*, possesses basic properties, and forms with acids well-defined salts.[2]

Chloro-molybdic bromide, $Mo_3Cl_4Br_2 + 3H_2O$, is obtained by heating the hydroxide or the chloride with hydrobromic acid. It crystallizes on cooling in glittering reddish-yellow plates which scarcely dissolve in water or in dilute hydrochloric acid. If the mother-liquor of this salt be evaporated well-formed reddish-yellow prisms having the composition, $Mo_3Cl_4Br_2 + 6H_2O$, are deposited. These dissolve in water, but are decomposed with separation of a yellow granular powder. Hydriodic acid forms corresponding compounds.

Brom-molybdic Hydroxide, $Mo_3Br_4(OH)_2 + 8H_2O$. When molybdenum dibromide is dissolved in dilute alkali and the solution allowed to stand exposed to the air, or when sal-ammoniac is added to the hot solution, the above compound is deposited in the form of golden-yellow glistening rhombohedrons closely approximating in form to the cube. These lose six molecules of water on drying over sulphuric acid, and change to a dark-red. At 100° they lose all their water, a fine red powder remaining behind.[3]

Brom-molybdic Chloride, $Mo_3Br_4Cl_2 + 3H_2O$, is obtained as a

[1] Liechti and Kempe, *Ann. Chem. Pharm.* clxix. 351.
[2] Blomstrand, *Journ. Pract. Chem.* lxxvii. 100.
[3] Atterberg, *Ber. Deutsch. Chem. Ges.* 1873, 1464.

pale-yellow powder on adding an excess of hydrochloric acid to the alkaline solution of the hydroxide.

Brom-molybdic Fluoride, $Mo_3Br_4F_2$, is prepared with hydrofluoric acid in the same way as the chloride, which it closely resembles.

Brom-molybdic Sulphate, $Mo_3Br_4SO_4 + 3H_2O$, can be obtained in the same way in the form of a yellow precipitate, whilst when the solution of the hydroxide is treated with ammonium molybdate and acetic acid, the *brom-molybdic molybdate* $Mo_3Br_4MoO_4 + H_2O$, is thrown down as a reddish-yellow precipitate.

446 *Molybdenum Sesquioxide*, Mo_2O_3, is formed when one of the higher oxides is treated with sodium amalgam, zinc, &c. When the trioxide is thus treated the colourless solution first becomes blue, then reddish-brown, and lastly black. The *hydroxide*, $Mo_2(OH)_6$, is obtained as a brownish-black precipitate by precipitating with ammonia, washing the precipitate with ammoniacal water, and drying in a current of hydrogen at 100°. When gently ignited in absence of air the water is evolved and the sesquioxide remains as a black mass (Berzelius). Molybdenum sesquioxide is likewise obtained in the form of a grey metallic powder by strongly igniting the trioxide in a current of hydrogen.[1] It is insoluble in acids, and even the hydroxide dissolves only with difficulty.

The Salts of the Sesquioxide are black or of a dark purple colour in concentrated solution, but when diluted they are transparent and of a purple tint. In the solid form the sesqui-salts are dark-grey or black. They have a styptic taste, oxidize slightly on exposure to the air, are precipitated by alkalis with formation of the hydroxide, and give a brown precipitate with sulphide of ammonium soluble in excess of the reagent. Sulphuretted hydrogen also precipitates them, though slowly. Phosphate of soda produces a brownish-black precipitate.

Molybdenum Sesquichloride, Mo_2Cl_6, is formed when the pure pentachloride is volatilized in a current of carbon dioxide, the tube being heated strongly at one point only. The sesquichloride deposits as a copper-red crystalline crust.[2] If the pentachloride be heated in a current of hydrogen to 250° the sesquichloride is also obtained in a form closely resembling red phosphorus (Liechti and Kempe). Heated in the air it forms a white woolly sublimate, whilst impure dichloride remains

[1] Svanberg and Struve, *Phil. Mag.* [3], xxx. 409–524.
[2] Blomstrand, *Journ. Pract. Chem.* lxxvii. 96.

behind. It is insoluble in cold water and is decomposed by boiling water. It likewise does not dissolve in hydrochloric acid, though it is easily soluble in hot nitric acid, whilst sulphuric acid dissolves it with a blue colour which on heating becomes green. If the hydroxide be dissolved in hydrochloric acid a brown liquid is obtained which on evaporation dries to a black pitch-like mass.

Molybdenum Sesquibromide, Mo_2Br_6, is formed by the action of bromine vapour on the heated metal. It sublimes in a mass of fine blackish-green needles which are insoluble in water though soluble in cold dilute nitric and in boiling hydrochloric acid. On boiling with alkalis the hydroxide is formed (Blomstrand).

447 *Molybdenum Dioxide,* MoO_2, is formed when the metal or the sesquioxide is gently heated in a current of air. If sodium trimolybdate be ignited for some hours in a current of hydrogen, and the residue treated with water, the dioxide remains behind in the form of a powder, having a brass-yellow colour.[1] If this salt be fused, and then heated with one-third its weight of zinc in small pieces, and the melted mass first treated with caustic potash, and then with hydrochloric acid, the same compound is obtained in the form of dark-blue prisms resembling sublimed indigo, which appear of a violet-red colour by transmitted light.[2] It is not attacked by caustic potash or hydrochloric acid, but when heated with nitric acid or on ignition in a current of steam, it is converted into the trioxide.

Molybdic Tetrahydroxide $Mo(OH)_4$, is obtained when a solution of the pentachloride or of ammonium molybdenum tetrachloride ide is precipitated with ammonia. On drying, the precipitate has a dark-red colour; it dissolves slowly in water, yielding a yellow or dark-red solution which reddens litmus, has a somewhat acrid and metallic taste, and is precipitated on the addition of salts. In closed vessels it decomposes after some time, forming a transparent jelly. The ignited dioxide does not dissolve in aqueous acids, although the hydroxide does so.

The Salts of the Dioxide are formed when an excess of molybdenum is treated with the corresponding acid, and then the requisite quantity of nitric acid added. The concentrated solutions are black, and on dilution they become of a bluish-green, greenish-yellow, dark-red, and lastly yellow colour. On

[1] Svanberg and Struve, *Journ. Prackt. Chem.* xliv. 257.
[2] Ullik, *Ann. Chem. Pharm.* cxliv. 204.

exposure to the air they absorb oxygen and become blue, whilst with zinc they give a black precipitate of $Mo_2(OH)_6$. With alkalis they yield a reddish-brown precipitate, and sulphuretted hydrogen, and sulphide of ammonium, give the same reactions with them as with the preceding salts.

Molybdenum Tetrachloride, $MoCl_4$, is obtained together with the dichloride, as has been stated, by heating the sesquichloride in an atmosphere of carbon dioxide. The tetrachloride volatilizes as a dark yellow vapour which condenses to a brown crystalline powder. When exposed to the air it becomes of a bluish-green colour and deliquesces to a brown liquid. It is only slowly soluble in hydrochloric acid, and dissolves in concentrated sulphuric acid with a bluish-green colour.

Molybdenum Tetrabromide, $MoBr_4$, is formed in small quantities in the preparation of the sesquibromide as black glistening needles which fuse when heated, volatilizing in brownish-red vapours. These readily decompose into bromine and dibromide, and in presence of air the compound deliquesces, forming a dark liquid, giving with more water a yellowish-brown solution.

Molybdenum Tetraiodide, MoI_4. The hydroxide dissolves in hydriodic acid, giving a red-coloured solution, which on spontaneous evaporation yields crystals which transmit red light and appear brown by reflected light.

Molybdenum Pentachloride, $MoCl_5$. This is the highest chloride of molybdenum, but it corresponds to no known oxide. It is formed by heating molybdenum or molybdenite in dry chlorine for some time, when bright metallic glistening black crystals are formed which melt at 194° and boil at 268°, giving a dark-red vapour which has a specific gravity of 9·4 to 9·53.[1] The compound fumes on exposure to moist air and becomes of a bluish-green colour, gradually deliquescing to a brown liquid which on dilution with water becomes colourless. Absolute alcohol and ether yield green solutions, and the chloride also dissolves in hydrochloric acid with evolution of heat.

OXYCHLORIDES OF MOEYBDENUM.

448 *Molybdenum Monoxytetrachloride*, $MoOCl_4$. This compound is formed by the action of chlorine on a moderately-heated mixture of carbon and molybdenum dioxide. It forms a dark-green

[1] Debray, *Compt. Rend.* lxvi. 732.

crystalline mass or, if obtained at a higher temperature, light-green plates having a metallic lustre. It melts and evaporates below 100°, solidifying to a green glistening mass and yielding a dark-red vapour. It is readily decomposed by water, deliquescing in moist air to a blue liquid, and this on addition of water gives a blue precipitate which becomes brown in presence of ammonia. As this decomposition by water eventually yields the blue oxide, Blomstrand [1] gives to this compound the complicated formula $Mo_9O_8Cl_{32}$, but its easy volatility does not support this formula.

α-Molybdenum Dioxydichloride, MoO_2Cl_2. This compound was first supposed to be molybdenum hexachloride, until H. Rose ascertained its true composition. It is formed by passing chlorine over the heated dioxide, when it sublimes as an amorphous mass. The same compound is also formed as a last oxidation-product when the chlorides of molybdenum are heated in the air. It can be fused only in closed vessels, and forms with water a colourless solution which has a bitter acid taste.

β-Molybdenum Dioxydichloride, MoO_2Cl_2. This compound, isomeric with the foregoing, is formed when molybdenum sesquioxypentachloride, a compound about to be described, is repeatedly sublimed in absence of air, the compound being obtained in thin yellow transparent quadratic tablets. When the mixture of the preceding compound and the sesquioxypentachloride is gently heated until the whole of the fusible portion is removed and the residue sublimed, the β-compound is obtained in the form of large and thick honey-yellow crystals,[2] which on repeated sublimation pass into the amorphous α-compound. These two isomeric oxychlorides correspond to the chromyl chlorides, and hence may be termed molybdenyl chlorides.

Molybdenum Sesquioxypentachloride, $Mo_2O_3Cl_5$. This compound is formed together with the amorphous molybdenyl chloride by heating the sesquichloride in a current of chlorine. It may be purified by slow sublimation in a current of hydrogen, and is thus obtained in dark-brown translucent well-formed prisms which probably belong to the rhombic system. It fuses easily and volatilizes as a reddish-brown vapour. Heated in contact with air it decomposes first into β-MoO_2Cl_2, and then

[1] *Journ. Pract. Chem.* lxxi. 460.
[2] Blomstrand, *Journ. Pract. Chem.* lxxi. 460.

into α-MoO_2Cl_2. In moist air it deliquesces, forming a blue liquid.

Molybdenum Sesquioxyhexachloride, $Mo_2O_3Cl_6$, is usually formed together with the green oxychloride, $MoOCl_4$, and crystallizes in well-formed dark-violet prisms which are ruby-red by transmitted light and which volatilize at a high temperature without fusion. It dissolves readily in water with evolution of heat, a white precipitate separating out which is soluble in a larger quantity of water.

Molybdenum Oxybromide or *Molybdenyl Bromide*, MoO_2Br_2, is formed when bromine vapour is passed over the heated dioxide, or when a mixture of molybdenum trioxide and boron trioxide is heated with bromide of potassium:

$$MoO_3 + B_2O_3 + 2KBr = MoO_2Br_2 + K_2B_2O_4.$$

It forms yellow tablets which deliquesce on exposure to air.

Molybdenum Oxyfluoride, MoO_2F_2, is only known in aqueous solution obtained by dissolving the trioxide in hydrofluoric acid. It forms double salts with the other fluorides of which many are soluble and crystallizable. They are prepared by dissolving the normal molybdates in hydrofluoric acid. Acid salts are also known which are obtained by the solution of the polymolybdates in hydrofluoric acid (Delafontaine).

Potassium Molybdic Oxyfluoride, $K_2MoO_2F_4 + H_2O$, forms small triclinic crystals which are permanent in the air and can be recrystallized from hot water. The acid salt, $K_2(F_3MoO_2)_2 + 2H_2O$, forms silky prisms which emit hydrofluoric acid on exposure to air.

MOLYBDENUM TRIOXIDE AND MOLYBDIC ACID.

449 *Molybdenum Trioxide*, MoO_3, occurs as molybdic ochre in crystalline or fibrous masses, as well as in an earthy powder or incrustation. It usually occurs together with molybdenite, and has probably been formed by its oxidation.

In order to prepare the trioxide in the pure state on the small scale the native sulphide may be heated in a combustion tube in a current of air until it is all oxidised, and the trioxide

sublimed.[1] On the larger scale it may be obtained by mixing the same powdered mineral with an equal weight of pure quartz sand and roasting the mixture on a flat iron plate. The roasted product is then boiled with dilute ammonia, and a small quantity of sulphide of ammonium added to the solution in order to precipitate the copper. The filtered liquid is then evaporated to dryness, and the residue again dissolved in dilute ammonia. Crystals of ammonium molybdate are obtained from the filtrate on concentration. These are decomposed by nitric acid, evaporated to dryness, and the residual trioxide well washed with water. Molybdenum trioxide can also be obtained from native lead molybdate by first treating the mineral with dilute hydrochloric acid in order to remove iron, zinc, &c., then decomposing it with hot concentrated hydrochloric acid, evaporating down and digesting with dilute ammonia, when ammonium molybdate remains in solution and can be crystallized out as has already been described.[2]

Thus prepared molybdenum trioxide is a white impalpable powder, which when heated becomes yellow; it melts at a red-heat to a dark yellow liquid, which, on cooling, solidifies to a yellowish-white fibrous crystalline mass, having a specific gravity of 4·39 (Schafarik). It volatilizes at very high temperatures when heated in closed vessels, but in the air it sublimes more easily, depositing small colourless transparent rhombic tablets. It dissolves in 500 parts of cold, and in about 960 parts of hot water. The solution reddens litmus paper, turns turmeric paper brown, and possesses a sharp metallic taste.

Molybdic Acid, $H_2MoO_4 + H_2O$, crystallizes out in yellow crusts when a solution of three parts of ammoniun molybdate is dissolved in twenty parts of water, and the same quantity of nitric acid of specific gravity 1·16 is added to the solution and the whole allowed to stand. The deposition of the acid frequently takes place only very slowly, and the addition of a crystal of the compound renders its separation more easy.[3]

When the solution of the trioxide in nitric acid is allowed to evaporate spontaneously a white crystalline powder separates, which on heating loses water (Berzelius). This probably consists of the anhydrous acid, H_2MoO_4, which was once obtained

[1] Wöhler, *Ann. Chem. Pharm.* c. 376. [2] Wöhler, *Mineralanalyse*, 146.
[3] Gmelin-Kraut, ii. 171.

by Ullik in the form of thin prismatic crystals by the decomposition of magnesium molybdate with nitric acid.

Collodial Molybdic Acid. When the hydrochloric solution of ammonium molybdate is dialysed, a yellow, strongly acid, astringent solution of molybdic acid remains behind, and this, on evaporation, yields a deliquescent gummy mass (Graham).[1]

Soluble Molybdic Acid. If ordinary molybdate of ammonia be precipitated with barium chloride, and the washed precipitate decomposed with the exact quantity of sulphuric acid, a colourless liquid is obtained, possessing an acid reaction and a metallic taste. This when dried over sulphuric acid solidifies to an amorphous mass, possessing a blue colour, owing to reduction, and is readily soluble in water, especially when slightly warmed.

Molybdenum trioxide not only combines with basic oxides to form molybdates, some of which possess very complicated constitutions, but it also acts as a base towards certain acids forming definite compounds. Thus, for instance, when hydrochloric acid gas is passed over molybdenum trioxide at a temperature of 150° to 200°, a white crystalline very volatile compound, $MoO_3 + 2HCl$, is formed. This, which is probably the hydroxychloride $MoO(OH)_2Cl_2$, is easily soluble in water and decomposes into its constituents when strongly heated. Again, if a solution of the trioxide be evaporated with concentrated sulphuric acid, colourless glistening crystals separate out having the composition $MoSO_6 = MoO_3SO_3$. These on heating emit sulphur trioxide and deliquesce on exposure to the air.

THE MOLYBDATES.

450 *Potassium Molybdate*, K_2MoO_4, is obtained by fusing molybdenum trioxide and carbonate of potash together in the right proportions. If the fused mass be dissolved in hot water, the solution allowed to cool, and the filtrate evaporated over sulphuric acid, the salt crystallizes out in small, usually microscopic, four-sided prisms, which are easily soluble in water. When hydrochloric acid is added drop by drop to a solution of molybdenum trioxide in carbonate of potash until a permanent turbidity is produced, a salt separates on standing, having the composition $K_6Mo_7O_{24}+4H_2O$.[2] This crystallizes in monoclinic

[1] *Chem. Soc. Journ.* xvii. 326.
[2] Delafontaine, *N. Arch. Sc. Phys. Nat.* xxiii. 5, xxx. 232.

prisms, and is decomposed by water with formation of the normal and the following salt.

Potassium Trimolybdate, $K_2Mo_4O_{10}+3H_2O$, forms pliable silky needles which dissolve slowly in cold, but more rapidly in hot water. If the salt be dissolved in molybdic acid prepared from barium molybdate a crystalline precipitate is formed, which dissolves in hot water, and the solution on cooling deposits glistening crystals having the composition $K_2Mo_4O_{13}+6H_2O$.

Sodium Molybdate, Na_2MoO_4, is formed when the trioxide and carbonate of soda are fused together in the proper proportions. The mass is dissolved in water, and evaporated to crystallization, when small acute rhombohedrons separate out, having the composition $Na_2MoO_4+2H_2O$. If a concentrated solution be allowed to crystallize below 6°, long prisms of the salt, $Na_2MoO_4 + 10H_2O$, having the appearance of glauber-salt, are deposited, and these lose moisture and pass into the foregoing compound on exposure to air.

Sodium Dimolybdate, $Na_2Mo_2O_7$, is formed when sodium carbonate is fused with twice as much trioxide as is needed to form the foregoing salt. The crystalline mass falls to pieces under water with formation of small needles which dissolve with difficulty in cold, and only slowly in hot water.

The salt $Na_6Mo_7O_{24}+ 22H_2O$, which crystallizes in large glistening monoclinic prisms, is obtained when the calculated quantity of the trioxide is dissolved in sodium carbonate and the solution allowed to evaporate spontaneously. It effloresces on exposure, and when heated in the air fuses in its own water of crystallization, which is given off at a higher temperature. When more strongly heated it melts with formation of the anhydrous salt, solidifying on cooling to long needles which are easily soluble in hot water, from which solution the original crystals can again be obtained.

Sodium Trimolybdate, $Na_2Mo_3O_{10}+7H_2O$, is formed in a similar way to the foregoing salt, and crystallizes in very fine needles. One hundred parts of water dissolve at 20° 3·878, and at 100° 137 parts of the salt.

Sodium Tetramolybdate, $Na_2Mo_4O_{13}+11H_2O$. This is obtained by the action of the calculated quantity of hydrochloric acid on the normal salt, and forms crusts consisting of small glistening crystals which dissolve with difficulty in cold, but readily in hot water.

The acid salt, $HNaMo_4O_{13} + 8H_2O$, which is obtained in a

similar way by the action of more hydrochloric acid, forms long glistening monoclinic crystals which are readily soluble in water, and effloresce on exposure to air.

Sodium Octomolybdate, $Na_2Mo_8O_{25} + 4H_2O$, is formed as a white powder by the action of a solution of sodium carbonate on the acid salt $HNaMo_8O_{25} + 4H_2O$, which latter salt is obtained by boiling the normal sodium molybdate with nitric acid, and also forms a white or yellowish powder

Sodium Decamolybdate, $Na_2Mo_{10}O_{31} + 12H_2O$, is a white crystalline powder obtained by heating the normal salt in a water-bath with sufficient hydrochloric acid to saturate the requisite quantity of sodium. It is difficultly soluble in water. If soluble molybdic acid be dissolved in the requisite quantity of sodium carbonate, the salt $Na_2Mo_{10}O_{31} + 21H_2O$, crystallizes in monoclinic prisms, and is soluble in cold water without decomposition.

451 *Ammonium Molybdate*, $(NH_4)_2MoO_4$, is produced when the trioxide, or an ammonium polymolybdate, is heated with excess of concentrated ammonia. It crystallizes in four-sided prisms which are decomposed by water. On evaporation of the solution of the trioxide in ammonia the *ordinary molybdate of ammonia*, $(NH_4)_6Mo_7O_{24} + 4H_2O$, crystallizes out in large colourless six-sided monoclinic prisms.

Ammonium Dimolybdate, $(NH_4)_2Mo_2O_7$, separates out on evaporating the mother-liquor of the normal salt in the form of a white crystalline powder.

Ammonium Trimolybdate, $(NH_4)_2Mo_3O_{10} + H_2O$, frequently occurs by the decomposition of a solution of the ordinary salt at a low temperature, when it separates out in silky needles difficultly soluble in cold- but readily so in hot-water.

Calcium Molybdate, $CaMoO_4$, is obtained by precipitating a solution of the ordinary ammonium salt containing an excess of ammonia with calcium chloride. It forms a white precipitate consisting of microscopic quadratic pyramids. If calcium carbonate be boiled with an excess of the trioxide and water, and the solution allowed to evaporate spontaneously, *calcium trimolybdate*, $CaMo_3O_{10} + 6H_2O$, is deposited. The salt $H_2CaMo_8O_{26} + 17H_2O$ crystallizes from a solution of the normal salt in the requisite quantity of hydrochloric acid. It is deposited in small oblique glistening prisms which are scarcely soluble in cold but readily dissolve in hot water.

Barium Molybdate, $BaMoO_4$, is a crystalline precipitate

difficultly soluble in acids. It is obtained in quadratic pyramids by fusing together sodium molybdate, barium chloride, and common salt.

When the ordinary ammonia salt is precipitated with barium chloride a flocculent precipitate of $Ba_3Mo_7O_{24} + 9H_2O$ is thrown down, which is slightly soluble in water. A compound, $BaMo_3O_{10} + 3H_2O$, having properties similar to the last salt, is obtained by precipitating a soluble trimolybdate. When barium carbonate is dissolved in soluble molybdic acid and the solution allowed to stand, oblique prisms of the salt $H_2BaMo_8O_{26} + 17H_2O$ are deposited; and if the normal salt be treated with dilute nitric acid the compound $BaMo_9O_{28} + 4H_2O$ is formed. This is incoluble in water and is not completely decomposed by acids, not even by sulphuric acid.

Magnesium Molybdate, $MgMoO_4 + 5H_2O$, is obtained by boiling magnesia with water and molybdenum trioxide, and evaporating the solution, when the salt separates out in long glistening transparent prisms. Magnesium molybdate forms with the molybdates of potassium and sodium double salts such as $K_2MoO_4 + MgMoO_4 + 2H_2O$, which appear to be isomorphous with the corresponding manganese and ferrous salts.

Lead Molybdate, $PbMoO_4$. This occurs native as wulfenite in orange-red transparent quadratic tables and octohedrons which have a specific gravity varying from 6 to 7. When one part of sodium molybdate is fused with six parts of lead chloride and four of sodium chloride in a closed crucible, bright-yellow translucent pyramids or tables of the artificial compound are obtained, which have a specific gravity of 6·811.[1] If a solution of a molybdate be added to lead nitrate the same compound is also obtained in the form of a white precipitate which melts at a very high temperature. We are not acquainted with any other lead molybdate.

Molybdenum Molybdates or *Blue Oxides of Molybdenum*. When the metal or a lower oxide of molybdenum is exposed for a certain time to the air a black mass is obtained, which, according to Berzelius, has the composition $Mo_5O_{11} = 4MoO_2 + MoO_3$. If molybdate of ammonia be heated with molybdenum trioxide to its melting-point, a violet-blue metallic lustrous powder of $Mo_3O_8 = MoO_2 + 2MoO_3$ is obtained. This compound may likewise be prepared by electrolysis of the fused trioxide when it forms in a crystalline mass which has a copper-red colour, and

[1] Schultze, *Ann. Chem. Pharm.*, cxxvi. 49; Manross, *ibid*, lxxxii. 358.

becomes blue on exposure to the air. On heating this compound a blue powder, $Mo_2O_5 = MoO_2 + MoO_3$, remains behind (Wöhler and Buff).

Hydroxides corresponding to the above are formed when the metal or molybdenum tetrahydroxide is moistened with water and exposed to the air, or when a solution of the tetrachloride is precipitated with ammonium molybdate, as also when the hydrochloric acid solution of a molybdate is heated with sugar and precipitated with common salt. The precipitate thus obtained has a dark-blue colour, and is soluble in water, to which it imparts a bitter metallic taste.

452 *Phosphomolybdic Acid*, $2H_3PO_4 + 22MoO_3$. This remarkable compound is obtained by boiling its ammonium salt with aqua-regia. On evaporating the solution it deposits in yellow triclinic prisms which contain twenty molecules of water. These dissolve very readily in water and, on spontaneous evaporation, cubes containing fifty molecules of water of crystallization separate out, whereas from a very concentrated nitric acid solution rhombic crystals are deposited, which contain 40 molecules of water. According to Debray,[1] who has recently investigated this acid and its salts, it only contains 20 MoO_3. The recent investigations of Rammelsberg,[2] however, confirm the formula given above.

Potassium Phosphomolybdate, $2K_3PO_4 + 22MoO_3 + 12H_2O$, is obtained by boiling the ammonia salt with caustic potash or by mixing the acid with solution of a potash salt, when it is deposited in four-sided prisms almost insoluble in water.

Ammonium Phosphomolybdate, $2(NH_4)_3PO_4 + 22MoO_3 + 12H_2O$. This salt was discovered by Gmelin,[3] but Sonnenschein[4] was the first to notice that this compound contained phosphoric acid as an essential constituent. It is formed when a solution of a molybdate is mixed with ammonia, and a small quantity of phosphoric acid in nitric acid solution added, or when the free acid is added to a strongly acid solution of the ammonia salt. Under these circumstances a canary-coloured yellow powder is thrown down. Pyro- and meta-phosphates do not yield this precipitate; it is only formed when they are converted into orthophosphates. When this change takes place slowly the compound is obtained in glistening yellow crystals

[1] *Compt. Rend.*, lxvi. 702.
[2] *Ber. Deutsch. Chem. Ges.*, x. 1776.
[3] *Handbook*, vol. iv. 68.
[4] *Journ. Prack. Chem.*, liii. 342.

(Debray).[1] It is almost insoluble in water and in dilute acids. It is also insoluble in nitric acid solution of ammonium molybdate. The presence of hydrochloric acid and chlorides, as well as of many organic acids, with the exception of acetic acid, retard the formation, whilst in presence of an excess of phosphoric acid no precipitation occurs.

It is easily soluble in alkalis, and the ammoniacal solution crystallises spontaneously in long glistening prisms or needles having the composition $(NH_4)_6(PO_4)_2 + 5MoO_3 + 7H_2O$. These are difficultly soluble in cold, but readily soluble in hot water, yielding a slightly acid liquid.

Phosphomolybdic acid also precipitates strongly acid solutions of the salts of rubidium, cæsium, thallium, and the organic alkaloids, but not solutions of sodium or lithium salts. The heavy metals are also not precipitated if a sufficient amount of free acid be present. This acid is used as a reagent for the alkaloids, or, in place of this, a liquid prepared by saturating a solution of sodium carbonate with molybdenum trioxide, and adding one part of phosphate of soda to every part of the trioxide, may be employed; this solution is evaporated to dryness, the residue fused, dissolved in water, filtered, and nitric acid added until the liquid becomes yellow.

MOLYBDENUM AND SULPHUR.

453 *Molybdenum Disulphide*, MoS_2, is found native as molybdenite in Sweden, Norway, Bohemia, Saxony, the Urals, at Caldbeck Fells in Cumberland, in Connecticut, California, and elsewhere. It commonly occurs in foliated masses or in scales, and sometimes in tabular hexagonal prisms, its general appearance being very similar to that of graphite, possessing a metallic lustre and pure lead-grey colour, and leaving a grey trace on paper. Molybdenite generally occurs embedded in or disseminated through granite, gneiss, zirconsyenite, granular limestone, and other crystalline rocks.

When the trioxide is fused with sulphur, or heated in a current of sulphuretted hydrogen, the same compound is obtained in the form of a glistening black powder, easily distinguished from graphite by the fact that when heated before the blowpipe it is incombustible and infusible, and that it oxidises when heated

[1] *Comptes Rendus*, lxvi. 702.

in the air with evolution of sulphur dioxide, and formation of molybdenum trioxide, and is readily oxidised by nitric acid and aqua-regia.

Molybdenum Trisulphide, MoS_3, is formed when sulphuretted hydrogen is passed into the concentrated solution of a molybdate, and hydrochloric acid added to the liquid. It may likewise be prepared by boiling the molybdate of an alkali metal for a short time with sulphide of ammonium, and then precipitating with dilute sulphuric acid. Thus obtained it is a reddish-brown precipitate which dries to a blackish-brown powder. On heating in absence of air it splits up into the foregoing compound and sulphur. It combines with basic sulphides to form thio-salts.

Potassium Thiomolybdate, K_2MoS_4, is formed when potassium molybdate is saturated with sulphuretted hydrogen. On evaporating the solution the compound crystallizes out in ruby-red four- or eight-sided prisms which have a green metallic lustre, and dissolve in water with a yellowish-red colour.

Ammonium Thiomolybdate, $(NH_4)_2MoS_4$, is obtained by dissolving the trisulphide in ammonium sulphide, and crystallizes in cinnabar-red scales.

Molybdenum Tetrasulphide, MoS_4. This substance forms compounds with many metallic sulphides known as the *perthiomolybdates*. Hydrochloric acid throws down from their solutions a fine red precipitate which dries to a mass having a metallic lustre. This when heated in a retort first evolves water and afterwards sulphur dioxide, and lastly sulphur, the disulphide remaining behind.

Potassium Perthiomolybdate, K_2MoS_5, is obtained by boiling a solution of potassium molybdate, which has been saturated with sulphuretted hydrogen, and molybdenum disulphide together. It forms small ruby-red transparent scales, and is with difficulty soluble in water.

MOLYBDENUM AND PHOSPHORUS.

Molybdenum Phosphide, Mo_2P_2, is obtained by strongly heating molybdenum trioxide and metaphosphoric acid in a carbon crucible. It forms a grey vesicular mass having a metallic lustre and containing crystals in the cavities. On ignition in the air it oxidizes slowly, and takes fire when thrown into fused nitre.

Detection and Estimation of Molybdenum.

454 Molybdenum trioxide and the molybdates may be detected inasmuch as the colourless hydrochloric acid solution when brought into contact with zinc becomes of a blue, green, and lastly dark-brown colour. The lower oxides, as well as their salts, can be readily transformed into the molybdates by oxidation. Molybdenum trioxide colours the blowpipe flame a yellowish green, and imparts to a bead of borax or microcosmic salt, a fine green colour in the reducing flame. Hydrochloric or nitric acid produces a curdy precipitate in solutions of a molybdate when not too dilute. This dissolves in an excess of acid, and even in a large quantity of water. A solution of ammonium molybdate in nitric acid becomes yellow-coloured on the addition of a few drops of sodium phosphate, and on warming a heavy yellow precipitate separates out. If some zinc be added even to a very dilute solution of a molybdate, and then hydrochloric acid, and a concentrated solution of potassium thiocyanate, the liquid becomes of a deep red colour, the red compound being dissolved on shaking up with ether.

Molybdenum trisulphide is slowly precipitated from an acid solution by sulphuretted hydrogen, and it dissolves readily in ammonium sulphide. When the solution containing ammonium thio-molybdate is acidified with dilute nitric acid, molybdenum trisulphide is thrown down.

In order to estimate molybdenum *quantitatively* it must be obtained as a neutral molybdate, which is then precipitated with a neutral solution of mercurous nitrate. The yellow precipitate which falls down is washed with a solution of mercurous nitrate, dried, and then either heated in a stream of hydrogen, when molybdenum dioxide is formed, or it is ignited with a weighed quantity of anhydrous lead oxide until all the mercury is driven off. The increase of weight of the residue gives then the amount of trioxide present.

The *atomic weight* of molybdenum was first accurately determined by Dumas,[1] by reducing the trioxide in hydrogen : as a mean of six experiments he arrived at the number 95·65. The same method carried out by Debray [2] gave the number 95·70 as a mean of three experiments, whilst Lothar Meyer [3] calculated

[1] *Ann. Chim. Phys.* [3], lv. 129. [2] *Compt. Rend.* lxvi. 732.
[3] *Liebig's Ann.* clxix. 360.

the number 95·86 from analyses of the chloride made by Liechti and Kempe, and lastly Rammelsberg by the reduction of the trioxide to metal obtained the number 95·96.[1]

TUNGSTEN, W = 183·5.

455 The minerals tungsten or heavy-stone, now termed scheelite or calcium tungstate, and wolfram (the *lupi spuma* of Agricola) were, up to the middle of the eighteenth century, both classed amongst the tin ores. In 1781, Scheele proved that tungsten was composed of lime combined with a peculiar acid, and in the same year, Bergman stated that, in his opinion, this acid is a metallic calx. Two years later the Spanish chemists Juan, José and Fausto d'Elhujar,[2] showed that this same acid is contained in the mineral wolfram combined with iron and manganese. They also succeeded in reducing metallic tungsten from the acid.

Tungsten is not a common metal, being found only in a few minerals, some of which occur, however, in fairly large quantities. The most important of these is wolfram, a tungstate of iron and manganese found in Cornwall, in Cumberland, on Rona in the Hebrides, in County Wicklow, at Zinnwald, and in many localities in the United States. Other important tungsten minerals are scheelite or calcium tungstate, $CaWO_4$, and scheelitine or lead tungstate, $PbWO_4$. In addition to these, tungsten occurs in the following somewhat rare minerals, wolfram ochre, WO_3; wolframite, $(MnFe)WO_4$; ferberite, $FeWO_4$; hübnerite, $MnWO_4$; and cupro-scheelite, $(CaCu)WO_4$.

In order to obtain the tungsten compounds from wolfram, a process proposed by Oxland in 1848 (see Tin) is generally adopted, the ore being fused with soda ash and sodium nitrate in a reverberatory furnace, and the soluble sodium tungstate being dissolved out and obtained by crystallisation.

456 *Metallic Tungsten.* This is prepared by calcining an intimate mixture of tungsten trioxide and carbon in a covered crucible. It may also be obtained by the reduction of the same oxide in a current of hydrogen or by the reduction of the chloride in vapour of sodium. It has, however, not been prepared in the

[1] *Ber. Deutsch. Chem. Ges.* x. 1776.

[2] *A Chemical Analysis of Wolfram and Examination of a New Metal, which enters into its Composition.* Translated from the Spanish by C. Cullen, to which is prefixed a translation of Mr. Scheele's analysis of the Tungsten, or heavy-stone, with Mr. Bergman's supplemental remarks. London, 1785.

coherent condition. In order to prepare the pure metal, the pure bright canary-yellow-coloured trioxide is ignited in a platinum or porcelain tube to bright redness in a current of dry and pure hydrogen. The metallic powder thus obtained possesses a light bright grey metallic lustre and has a specific gravity at 4° of 19·129 (Roscoe).[1] The specific gravity of the metal, according to earlier observers, was found to be considerably lower.

Metallic tungsten does not undergo any oxidation either in dry or moist oxygen at the ordinary temperature, even when exposed for many months. At a red-heat the powdered metal burns in air or oxygen, being converted into the trioxide. When thrown into chlorine it does not burn but combines with this element when heated in it at a temperature of 250° to 300°. It also combines with bromine and more difficultly with iodine. Water does not act upon metallic tungsten at the ordinary temperature, but a current of steam passed over tungsten heated to redness oxidizes the metal to a mixture of the blue oxide and the trioxide. Treated with boiling solution of potash, tungsten is oxidized, tungstate of potash being formed and hydrogen disengaged. Nitric acid only attacks tungsten slowly, but it is oxidized rapidly in contact with aqua regia.

Tungsten Steel. Many suggestions have been made for improving the quality of tool-steel by the addition of tungsten, inasmuch as this is said to improve the quality, hardness, and tenacity of the metal, but it appears that this application has not proved commercially successful.

TUNGSTEN AND CHLORINE.

457 Four compounds of tungsten and chlorine are known, viz.:

(1) Tungsten dichloride . . . WCl_2.
(2) Tungsten tetrachloride . . WCl_4.
(3) Tungsten pentachloride . . WCl_5.
(4) Tungsten hexchloride . . WCl_6.

Tungsten Dichloride, WCl_2. This body may be obtained in pale-grey crusts by reducing the hexchloride at a moderately high temperature in hydrogen. It is, however, best prepared by heating the tetrachloride in a current of carbon dioxide. For this purpose the temperature of a moderately hot zinc bath is

[1] *Mem. Lit. and Phil. Soc. of Manchester*, [3] v. 77.

used. The dichloride is a non-volatile loose grey powder without lustre or crystalline structure. It alters perceptibly on short exposure to the air and dissolves slightly in water forming a brown solution. The remainder is converted into the brown oxide, a slow evolution of hydrogen occurring (Roscoe).

Tungsten Tetrachloride, WCl_4, is formed by the incomplete reduction of the hexchloride or pentachloride by hydrogen, forming the non-volatile residue obtained by the distillation of the hexchloride in hydrogen. In order to obtain it in the pure state a mixture of hexa- and pentachloride is distilled at a low temperature in a bath of sulphuric acid in a current of dry hydrogen or carbon dioxide and the volatile pentachloride distilled back again once or twice over the residue to saturate up to the tetrachloride the lower chlorides or metal which are also formed. The tetrachloride of tungsten is a loose soft crystalline powder of a greyish-brown colour. It is highly hygroscopic, though not so much so as the pentachloride. It is partially decomposed by cold water into the brown oxide and hydrochloric acid. The tetrachloride is non-volatile and infusible under ordinary pressure, but on heating it decomposes into pentachloride, which distils off, and dichloride, which remains behind. On heating in hydrogen to a temperature above the melting-point of zinc the tetrachloride is reduced to metallic tungsten, some of which is deposited as a black tinder-like powder and undergoes spontaneous ignition on exposure to air (Roscoe).

Tungsten Pentachloride, WCl_5. This compound is formed by the incomplete reduction of the hexchloride in a current of hydrogen. If the temperature be kept but slightly above the boiling-point of the hexchloride the dark-red colour of its vapour is seen to disappear and a light greenish-coloured vapour takes its place, and this soon condenses either to black drops or to long shining black needle-shaped crystals. After two or three distillations in hydrogen a pure volatile product is obtained. For the production of the pentachloride it is, however, more convenient to reduce the hexchloride at a higher temperature, when a further loss of chlorine takes place, the solid non-volatile tetrachloride remaining behind and the volatile pentachloride distilling over. The latter compound only requires redistillation in order to obtain it in the pure state. Tungsten pentachloride crystallizes in long black shining crystals, but if quickly condensed the crystalline powder possesses

a dark-green colour resembling potassium manganate. It is extremely hygroscopic, the crystals becoming instantly covered with a dark golden-green film on exposure to air, and the small particles converted into liquid. The crystals do not decrepitate on cooling like those of the hexchloride. On treatment with large quantities of water, the pentachloride forms an olive-green solution, although the greater part is at once decomposed into the blue oxide and hydrochloric acid. The melting-point of tungsten pentachloride is 248°, and its point of solidification 242°, and it boils at 275°·6. The vapour density of tungsten pentachloride taken in sulphur vapour at 440° was found to be 186°·5 (H = 1), whilst in mercury vapour at 350° it was found to have a density of 177·8 (Roscoe). The formula WCl_5 requires a vapour density of 180·7.

Tungsten Hexchloride, WCl_6. This substance is prepared by heating metallic tungsten in an excess of dry and pure chlorine. It is necessary for the preparation of the pure compound that every trace of oxygen and of moisture be excluded, as otherwise some red oxychloride is invariably formed, and this cannot easily be separated from the hexchloride by distillation. Metallic tungsten takes fire at a moderate heat in dry chlorine and the action goes on by itself until all the chlorine has disappeared.

In order to obtain the hexchloride in quantity the metal is first ignited in a current of dry hydrogen; then the hydrogen is completely displaced by a current of dry carbon dioxide and lastly chlorine free from air substituted, and the tube or retort moderately heated. At the commencement of the operation a slight sublimate of red needle-shaped crystals of the oxychloride is frequently formed owing to the unavoidable presence of traces of oxygen, but this is easily driven to the end of the tube beyond the point at which it is intended to collect the hexchloride. On raising the temperature of the metal, a granular sublimate of dark-violet opaque crystals of the hexchloride makes its appearance, and if in large quantity the hexchloride collects as a blackish-red liquid. In order to saturate this liquid, it is slowly distilled in a current of chlorine. The dark violet crystals decrepitate on cooling and the crystalline mass thus readily breaks up to a powder.

When pure, the solid hexchloride does not undergo any change even in moist air, but in the presence of the slightest trace of oxychloride it at once absorbs moisture, evolving copious fumes

of hydrochloric acid and changing in colour from violet to brown. Water does not act upon the pure hexchloride, but on boiling decomposition occurs. If, however, the oxychloride be present the whole is suddenly decomposed by cold water into a greenish oxide. It is soluble in carbon disulphide, crystallizing from the solution in six-sided plates.

The melting-point of the hexchloride is 275° and its point of solidification 270°; it boils under a pressure of 759·5 mm. at 346°·7. The vapour density of tungsten hexchloride has been determined in sulphur vapour and in mercury vapour; at 440°, the mean experimental density is 168·8, whilst at 350° the density is 190·9, the calculated density being 198·5. The alteration of the density from 191 at 350°, only 3° above the boiling-point, to 169 at 440° points to the fact that dissociation occurs. That this is the case is shown by the fact that when a current of dry carbon dioxide is passed through the fused hexchloride a continuous liberation of the chlorine takes place, whereas the pentachloride treated in the same way does not undergo a similar decomposition.

458 *Tungsten Oxychlorides.* The *monoxychloride*, $WOCl_4$, and the *dioxychloride* WO_2Cl_2, have been studied by Blomstrand and Riche. The dioxychloride is best obtained by passing chlorine over the brown oxide. Combination takes place at a moderate heat, the oxide becoming covered with a whitish crust which on increase of temperature distils off without melting, condensing in small square scales of a light lemon-yellow colour. The dioxychloride volatilises at a temperature approaching redness with partial decomposition; the crystals do not fuse and are not acted upon by moist air or cold water. Even when boiled with water the dioxychloride is not completely decomposed.

The splendid red needle-shaped crystals of the monoxychloride, first prepared by Wöhler, are best obtained by passing the vapour of a chloride over heated oxide or dioxychloride, in a current of chlorine:

$$WO_3 + 2WCl_6 = 3WOCl_4.$$

The crystals melt at 210°·4 and solidify at 207°·4, and the liquid boils at 227°·5, forming a red vapour rather lighter coloured than that of the hexchloride. On repeated distillation over red-hot charcoal in a current of chlorine the hexchloride is formed. On exposure to air the monoxychloride becomes at once covered

with a yellowish crust of tungstic acid. The vapour density at 350° is found to be 171·5 and at 440° 173, the theoretical density being 171 (Roscoe).

TUNGSTEN AND BROMINE.

459 Bromine acts rapidly on red-hot tungsten, forming dark bromine-like vapours, which condense to a crystalline sublimate. Special precautions similar to those taken in the preparation of the chlorides must also be employed for the bromides, as the oxybromides formed in the presence of air and moisture possess almost the same colour as the bromide, and therefore the detection of the impurity is not so easy as is the case with the chloride.

Tungsten Dibromide, WBr_2, is formed by the reduction in hydrogen of the pentabromide, heated in a bath of fused zinc chloride. A residue of non-volatile dibromide remains in the form of a bluish-black velvety crystalline powder.

Tungsten Pentabromide, WBr_5. By the action of an excess of bromine on tungsten a penta- and not a hexbromide is obtained. Indeed the pentabromide itself evolves bromine on standing. The pentabromide forms dark crystals having a metallic lustre resembling iodine, melting at 276°, solidifying at 273°, and boiling at 333°. It is at once decomposed by an excess of water into hydrobromic acid and the blue oxide. When the pentabromide is heated in a current of hydrogen, the metal is formed in the state of pyrophoric powder.

Tungsten Oxybromides, corresponding to the oxychlorides, exist. The dioxybromide WO_2Br_2, is formed by passing bromine vapour over red-hot tungsten dioxide. It forms light-red transparent crystals which yield a yellow powder. They do not melt, but volatilize at a temperature approaching a red-heat, and they are not acted upon by water. The monoxybromide $WOBr_4$, is formed under the same circumstances as the last-named compound as brownish-black shining needles which are readily fusible and can be separated from the dioxybromide by gently heating, when the latter compound remains behind. It melts at 277°, boils at 327°·5, and is decomposed by contact with water.

TUNGSTEN AND IODINE.

Tungsten Di-iodide, WI_2, is obtained in the form of green metallic scales, when iodine vapour is passed over the metal heated to redness (Roscoe).

TUNGSTEN AND FLUORINE.

Tungsten trioxide dissolves in strong hydrofluoric acid, but on evaporation the oxide crystallizes out unchanged. Neither a fluoride nor an oxyfluoride of tungsten is known in the free state, but a compound $K_2F_4WO_2$, is obtained when normal potassium tungstate is dissolved in hydrofluoric acid, and this compound is isomorphous with the corresponding molybdenum oxyfluoride.

TUNGSTEN AND OXYGEN.

460 Tungsten forms two definite oxides: tungsten dioxide WO_2, and tungsten trioxide WO_3. These combine together to form compounds analogous to the blue oxides of molybdenum (p. 196).

Tungsten Dioxide, WO_2. This oxide is formed when a current of hydrogen is passed over the trioxide, WO_3, at a dull red-heat. It may also be obtained in the wet way by reducing the trioxide, mixed with hydrochloric acid, by means of metallic zinc. In preparing it in the dry way care is needed, as if the temperature be too high metallic tungsten is formed, whereas if the heat be not sufficient, the intermediate blue oxide is produced. Tungsten dioxide is a brown powder of specific gravity, 12·1, which has a copper-red colour when crystalline trioxide is employed for its preparation. It is strongly pyrophoric, and must be cooled in hydrogen for some time before it is exposed to the air. It is slightly soluble in concentrated hydrochloric acid and sulphuric acid, yielding purple solutions. Oxidizing agents convert it rapidly into the trioxide. It dissolves in potash with disengagement of hydrogen and the production of potassium tungstate:

$$WO_2 + 2KOH = K_2WO_4 + H_2.$$

Tungsten Trioxide, WO_3. This oxide occurs native as wolframine, a yellow powder found together with other tungsten minerals in Cumberland, near Limoges, in Connecticut, and in North Carolina. In order to prepare the trioxide, finely powdered wolfram is digested for a long time with hydrochloric acid, the mixture frequently shaken, the acid renewed, and a little nitric acid added towards the end of the process to oxidize the iron. This is continued until the acid has dissolved out the whole of the iron and manganese and the brown powder has become yellow coloured. The insoluble portion, consisting of tungsten trioxide and undecomposed wolfram and quartz, after being well washed, is shaken up with a solution of ammonia, which dissolves the liberated tungstic acid. The solution is crystallized and the crystals are converted into the trioxide by ignition in the air. Wöhler converts the wolframite into calcium tungstate by fusion of the finely powdered mineral for an hour with twice its weight of chloride of calcium and then lixiviating, when calcium tungstate remains behind. This is then decomposed by nitric acid, and tungsten trioxide is obtained by igniting the yellow precipitate thus thrown down. The native tungstate of calcium (scheelite) can also be decomposed in this way.

Tungsten trioxide is a bright canary-yellow coloured powder which becomes dark-orange on heating, but regains its bright yellow colour on cooling. A very slight admixture of sodium salt imparts to the oxide a greenish tint which no amount of oxidation can remove (Roscoe). It also becomes greenish on exposure to light. Tungsten trioxide has been obtained in the crystalline state by Debray, by igniting a mixture of tungstate and carbonate of sodium in a current of hydrochloric acid, when the trioxide is obtained in olive-green rectangular prisms which sublime at a white heat. The crystalline trioxide has also been prepared by heating hydrated tungstic acid with borax in a porcelain furnace (Nordenskjöld). The specific gravity of tungsten trioxide thus obtained is 6·34.

When heated in a current of hydrogen to 250° the trioxide is converted into the blue oxide, $2WO_3+WO_2$, and if the heat be raised to dull redness the brown oxide, WO_2, is formed, whilst at a higher temperature the metal is obtained. Acted upon by reducing agents such as zinc and hydrochloric acid, stannous chloride, or organic matter, tungsten trioxide is transformed successively into the blue and brown oxides. Tungsten

trioxide is soluble in the fixed alkalis and ammonia as well as in the alkaline carbonates, which it decomposes, giving rise to the tungstates. It is insoluble in water and acids; it dissolves, however, in small quantities in concentrated hydrochloric and hydrofluoric acids.

TUNGSTIC ACIDS AND THE TUNGSTATES.

461 Two modifications of tungstic acid exist, termed *normal-* and *meta-tungstic acid;* and the tungstates, many of which possess a complicated constitution, may be likewise divided into two corresponding classes, the ordinary- or normal-tungstates and the metatungstates.

Tungstic Acid, H_2WO_4. When a solution of a tungstate is precipitated by an acid in the cold, a white precipitate is thrown down consisting of hydrated tungstic acid, $H_2WO_4+H_2O$. This is soluble in water, possesses a bitter taste and reddens litmus. If, on the other hand, a solution of a tungstate is treated with an excess of hot acid, anhydrous tungstic acid, H_2WO_4, separates out as a yellow powder, and this is insoluble in water and in all acids except hydrofluoric acid. If pure tungsten hexchloride be exposed to the action of moist air, the red monoxychloride is first formed and this soon passes into a fine flocculent mass of tungstic acid.

The tungstates are insoluble in water with the exception of those of the alkali-metals; and, even of these, some tungstates of potassium and ammonium are only sparingly soluble. The tungstates of the alkaline-earth metals, and of the heavy metals, are mostly amorphous powders, but they may be obtained in the crystalline state by double decomposition at a high temperature.

Metatungstic Acid, $H_2W_4O_{13}+7H_2O$. The salts of this acid were discovered by Margueritte,[1] but the acid was first prepared by Scheibler.[2] For this purpose the barium salt is decomposed by dilute sulphuric acid or the lead salt with sulphuretted hydrogen. Metatungstic acid crystallizes in small yellow octohedrons which lose their water of crystallization at 100°, and on ignition are converted into the trioxide. They are readily soluble in water and the solution possesses a harsh bitter taste. When the solution is concentrated by boiling, a white hydrate is deposited and afterwards the trioxide separates out. The

[1] *Ann. Chim. Phys.* [3], xvii. 475. [2] *Journ. Pract. Chem.* lxxxiii. 310.

metatungstates of the alkali-metals are formed when the ordinary tungstates are boiled with tungstic acid until the filtrate does not precipitate on addition of hydrochloric acid. The metatungstates of the other metals are mostly easily soluble in water, and are best prepared by double decomposition of the barium salt with the corresponding sulphate or carbonate. The warm solutions usually yield the salts in amorphous masses when evaporated, but when concentrated over sulphuric acid they frequently crystallize. The metatungstates possess a bitter taste and do not yield a precipitate on addition of an acid, though on continued boiling ordinary tungstic acid is deposited.

462 *Colloidal Tungstic Acid.* This modification of tungstic acid was discovered by Graham.[1] It is obtained by dialysing a 5 per cent. solution of tungstate of sodium to which a sufficient quantity of hydrochloric acid has been added to neutralize the soda. After several days, the liquid remaining on the dialyser is found to possess a bitter astringent taste and does not gelatinize on the addition of acids, even on boiling. On evaporating in a vacuum a colourless, vitreous, transparent, gum-like mass is obtained, and this can be heated to 200° without losing its solubility, whilst at a red-heat it is transformed into tungsten trioxide, losing 2·4 per cent. of water. When moistened with water the colloidal acid becomes pasty and adhesive like gum, dissolving completely in one-quarter of its weight of water.

Potassium Tungstates. The *normal salt*, K_2WO_4, is obtained by adding tungsten trioxide little by little to its own weight of fused carbonate of potash. On cooling a solution of the fused mass in hot water, or on allowing the solution to evaporate slowly at the ordinary temperature, normal potassium tungstate crystallizes in large acicular anhydrous crystals or in large prismatic crystals, $K_2WO_4 + 2H_2O$ (Marignac). When the normal salt is boiled with a small quantity of water, or when tungsten trioxide is added to its boiling solution until no more dissolves, glistening scales of the acid salt, $K_{10}W_{12}O_{41} + 11H_2O$, are deposited. These dissolve more readily in hot than in cold water, and the solution has an acrid taste and acid reaction. When alcohol is added to the aqueous solution a precipitate is formed; this dissolves on warming but on cooling deposits scales of *Potassium metatungstate*, $K_2W_4O_{13} + 5H_2O$; a second hydrated salt containing eight molecules of water, crystallizing in octohedrons, is obtained from the mother-liquor of the normal tungstate.

[1] *Journ. Chem Soc.* xvii. 325.

463 *Sodium Tungstates.* The *normal salt*, $Na_2WO_4 + 2H_2O$, is prepared like the potassium salt, and is obtained on the large scale by fusing wolfram together with soda-ash. It crystallizes in thin rhombic prisms which dissolve in four parts of cold and in two parts of boiling water. The solution possesses a bitter taste and has an alkaline reaction. The crystals do not undergo alteration in the air and they are insoluble in alcohol. When heated to 200° it becomes opaque and loses its water, and at a red-heat fuses to a transparent liquid which crystallizes on cooling.

In addition to the normal salt the following *polytungstates* of sodium are known:[1]

$Na_2W_2O_7 + 2H_2O.$
$Na_4W_3O_{11} + 7H_2O.$
$Na_4W_5O_{17} + 11H_2O.$
$Na_6W_7O_{24} + 16H_2O.$
$Na_6W_7O_{24} + 21H_2O.$
$Na_{10}W_{12}O_{41} + 21H_2O.$
$Na_{10}W_{12}O_{41} + 25H_2O.$
$Na_{10}W_{12}O_{41} + 28H_2O.$

These salts are all soluble in water and crystallizable. The salt, $Na_{10}W_{12}O_{41}$, sometimes termed *sodium paratungstate*, is prepared on the large scale by roasting wolfram with soda-ash and lixiviating the fused mass. The boiling solution is then nearly neutralized with hydrochloric acid and the salt allowed to crystallize at the ordinary temperature when the compound containing twenty-eight molecules of water deposits in large triclinic crystals. At a higher temperature it crystallizes with less water than the above. This salt is sometimes used in place of stannate of sodium as a mordant in dyeing and calico-printing, and is also employed for rendering cotton, linen, &c., uninflammable.[2]

Sodium Metatungstate, $Na_2W_4O_{13} + 10H_2O$, is formed by prolonged boiling of the normal salt with tungsten trioxide. It crystallizes in octohedrons probably belonging to the regular system. It is very efflorescent. Cold water dissolves 10·69 times its weight of this salt and boiling water dissolves it in all proportions. It loses its water at a red-heat (Marignac and Scheibler).

[1] Marignac, *Ann. Chim. Phys.* [3] lxix. 39.
[2] Versmann, *Reports of the Juries of the Exhibition of* 1862.

464 *Ammonium Tungstates.* The normal salt is not known. When a solution of tungstic acid in ammonia is allowed to evaporate over caustic lime, warty concretions of $(NH_4)_8W_3O_{13} + 3H_2O$ are sometimes deposited, which easily give off ammonia. Needle-shaped crystals or tablets having the composition $(NH_4)_6W_7O_{24} + 6H_2O$ are, however, usually deposited, whilst sometimes small triclinic crystals of $(NH_4)_4W_5O_{17} + 5H_2O$ likewise occur. If, however, the ammoniacal solution of the trioxide be allowed to evaporate whilst warm, monoclinic crystals of $(NH_4)_{10}W_{12}O_{41} + 5H_2O$ separate out. When tungsten trioxide is boiled with ammonia, quadratic prisms of *ammonium metatungstate* $(NH_4)_2W_4O_{13} + 8H_2O$ are obtained. These are very soluble and effloresce quickly on exposure to the air. Besides these many other ammonium tungstates have been prepared (Marignac).

Normal Calcium Tungstate, $CaWO_4$. This occurs native as scheelite in vitreous yellowish-white quadratic pyramids. Some of its chief localities are Zinnwald, Caldbeck Fell in Cumberland, Piedmont, Dalecarlia, in the Vosges, at Huntingdon in Connecticut, and at the Mammoth mining district in Nevada. The crystals usually contain iron and are found in crystalline rocks in connection with tin-ore, topaz, apatite, wolfram, &c.

It is prepared artificially as a white insoluble precipitate by mixing solutions of calcium chloride and a normal tungstate, and can be obtained in the crystalline form of scheelite by heating the precipitate mixed with lime in a current of hydrochloric acid. If a hot solution of metatungstic acid be saturated with calcium carbonate, calcium metatungstate, $CaW_4O_{13} + 10H_2O$, is obtained, crystallizing in small quadratic octohedrons.

Normal Barium Tungstate, $BaWO_4$, is obtained by fusing together the sodium salt with common salt and barium chloride, in the form of lustrous colourless crystals isomorphous with scheelite. *Barium Metatungstate,* $BaW_4O_{13} + 9H_2O$, is obtained by mixing hot saturated solutions of the sodium salt and barium chloride with addition of some hydrochloric acid. It forms large quadratic pyramids which may be easily purified by recrystallization from hydrochloric acid solution. If baryta water be added to the aqueous solution of the salt, needle-shaped crystals of $2BaWO_4 + H_2O$ are deposited.

Lead Tungstate, $PbWO_4$, occurs as stolzite at Zinnwald in Bohemia, at Bleiberg in Carinthia, in Chili, and at Southampton,

Massachusetts. It crystallizes in red translucent quadratic pyramids having a specific gravity of 7·87 to 8·13.

Ferrous Tungstate, $FeWO_4$, occurs as the mineral farberite in Spain, closely resembling the commoner mineral wolfram, which contains manganese as an isomorphous constituent, $(FeMn)WO_4$. This latter occurs in Cornwall, Cumberland, in Ireland, France, in the Erzgebirge, and in various parts of the United States. Wolfram crystallizes in the rhombic system in dark grey or brownish-black prisms having a metallic lustre and a specific gravity of 5 to 5·5.

Manganese Tungstate, $MnWO_4$, is found as hübnerite in Nevada in a vein from three to four feet wide.

COMPOUNDS OF TUNGSTATES WITH TUNGSTEN DIOXIDE.

465 These singular compounds, formed by the reduction of the tungstates, have been employed as bronze-powder substitutes.

Tungsten-potassium Bronze. The compound $K_2W_3O_9 = K_2W_2O_7 + WO_2$ is obtained by adding tungsten trioxide to fused normal potassium tungstate until it no longer dissolves. The product is then gently heated in a stream of hydrogen and afterwards lixiviated with water, hydrochloric acid, and caustic potash, and lastly again with water. It forms small dark-blue needles which possess a copper-red lustre. A compound crystallising in fine deep-blue copper-lustrous quadratic prisms and pyramids, having the composition $K_2W_5O_{12} = K_2WO_4 + 4WO_2$, is obtained by passing a galvanic current through fused potassium polytungstate. This is not altered by the action of aqueous alkalis and acids.

Tungsten-sodium Bronze, $Na_2W_3O_9 = Na_2W_2O_7 + WO_2$. This beautiful compound was first prepared by Wöhler by a similar method to that described for the potassium compound. It is also obtained when a polytungstate is fused with tin and the mass treated with caustic soda and hydrochloric acid. It forms fine golden cubes, which have a specific gravity of 6·617, and conduct electricity well. On ignition in the air it oxidizes and fuses. It is not attacked by any acid except hydrofluoric acid, nor is it acted upon by alkalis.

Phospho-tungstic Acids. Like molybdic acid, tungstic acid combines with phosphoric acid to form complicated compounds. The sodium salts are obtained by boiling a sodium tungstate

with phosphoric acid. If the ordinary commercial tungstate of soda be used, and barium chloride be added to the product, a precipitate is obtained which, when decomposed by sulphuric acid, yields phospho-decatungstic acid, $H_{11}PW_{10}O_{38} + 8H_2O$, which crystallizes in cubes, and, like phospho-molybdic acid, possesses the property of precipitating the alkaloids,[1] and it may be used as a reagent for this purpose.

TUNGSTOSILICIC ACIDS.

466 These peculiar compounds were discovered and investigated by Marignac,[2] who gives the following names and formulæ:

Silicodecitungstic acid, $4H_2OSiO_2 10WO_3$.
Tungstosilicic acid, $4H_2O 12WO_3SiO_2$.
Silicoduodecitungstic acid, $4H_2OSiO_2 12WO_3$.

Silicodecitungstic Acid, $H_8W_{10}SiO_{36} + 3H_2O$. To prepare this acid gelatinous silica is boiled with ammonium polytungstate and the solution evaporated, ammonia being added from time to time. Thus the ammonium salt, $(NH_4)_8SiW_{10}O_{36} + 8H_2O$, is obtained in short rhombic prisms which are soluble in water and precipitated by silver nitrate. The precipitate is washed and decomposed by hydrochloric acid. On evaporating the filtrate in a vacuum the acid is left as a yellowish, glassy mass, which on exposure to air splits into fragments, which then deliquesce. Its salts have not been carefully examined.

On dissolving it in water and evaporating the solution some silicic acid separates out and the thick mother-liquor yields short triclinic prisms of *tungstosilicic acid,* $H_8W_{12}SiO_{42} + 20H_2O$, which are readily soluble in water and alcohol. It forms both normal and acid salts.

Normal Potassium Tungstosilicate, $K_8W_{12}SiO_{42} + 20H_2O$, crystallizes in ill-defined, rhombic prisms.

Acid Potassium Tungstosilicate, $H_4K_4W_{12}SiO_{42} + 7H_2O$, occurs in two different forms, which crystallize from the same solution, and if one form be dissolved in water, the second form frequently crystallises out.

The *a*-compound forms transparent, thick, rhombic prisms;

[1] Scheibler, *Ber Deutsch. Chem. Ges.* v. 801; Gibbs, *ibid.* x. 1385.
[2] *Ann. Chim. Phys.* [4], iii. 5.

the β-compound crystallizes in silky, soft, six-sided rhombic plates.

Silicoduodecitungstic or *Silicotungstic Acid*, $H_8SiW_{12}O_{42} + 29H_2O$. The salts of this acid are formed by boiling gelatinous silicic acid with the polytungstates of the alkali metals. To obtain the acid the salts are precipitated with mercurous nitrate and the washed precipitate is decomposed by hydrochloric acid. It crystallizes in large quadratic pyramids, which readily dissolve in water, alcohol, and ether. On gently heating it melts in its water of crystallization and rhombohedrons of $H_8SiW_{12}O_{42} + 22H_2O$ are deposited. These are also formed by adding a little hydrochloric acid to its solution and concentrating it.

It forms normal, acid, and double salt which, with the exception of the mercurous salt, are all soluble in water. Boiling hydrochloric acid converts the normal salts into acid salts without decomposing them further; alkalis decompose their solutions with the separation of silicic acid.

Normal Potassium Silicotungstate, $K_8SiW_{12}O_{42} + 14H_2O$, forms hard granular crusts, consisting of prisms closely resembling cubes. It yields two acid salts; $H_4K_4SiW_{12}O_{42} + 16H_2O$ forming transparent, glistening, hexagonal crystals, and $2H_5K_3SiW_{12}O_{42} + 25H_2O$ crystallising in monoclinic prisms.

TUNGSTEN AND SULPHUR.

467 *Tungsten Disulphide*, WS_2, is obtained by the action of sulphur, sulphuretted hydrogen, or carbon disulphide on ignited metallic tungsten. It is also prepared by heating tungsten trioxide in a crucible with six times its weight of cinnabar. It forms tender, soft, black, needle-shaped crystals, which soil the fingers like graphite.

Tungsten Trisulphide, WS_3, is obtained only in the wet way, by dissolving tungsten trioxide in sulphide of ammonium and precipitating with an acid, or by saturating an aqueous solution of an alkaline tungstate with sulphuretted hydrogen, and acidifying When dry it is black, yielding a liver-coloured powder. It dissolves slowly in cold water, and is precipitated by sal-ammoniac and acids. It is easily dissolved by potassium carbonate, and also by ammonia. It is reduced when heated with cyanide of potassium to the disulphide, this latter compound being unaltered by fusion with potassium cyanide.

The Sulphotungstates. The sulphotungstates of the alkali-metals and alkaline earth metals, are prepared by dissolving the trisulphide in the corresponding hydrosulphide, or by treating the corresponding tungstate with sulphuretted hydrogen. The ammonium salt $(NH_4)_2WS_4$, is deposited from concentrated solution in yellowish-red crystals ; the potassium salt, K_2WS_4, forms anhydrous yellow crystals, whilst the sodium salt, Na_2WS_4, crystallizes with difficulty.

TUNGSTEN AND NITROGEN.

According to Wöhler[1] a nitride or amide of tungsten is formed when the vapours of chloride of tungsten and sal-ammoniac are passed through a red-hot tube. The inner surface of the heated tube is found to be covered with a black specular semi-metallic coating, having the composition $W_3N_6H_4$. Heated in hydrogen this compound is converted into a grey powder having the composition $W_3N_4H_4$, and this when strongly ignited in ammonia yields tungsten nitride W_3N_2.

TUNGSTEN AND PHOSPHORUS.

Phosphorus and tungsten combine directly when the finely powdered metal is heated to redness in phosphorus vapour, a dark green powder, of the composition W_3P_4, being formed. Another compound, W_4P_2, is obtained in beautiful crystalline geodes when a mixture of phosphorus pentoxide and tungsten trioxide in the proportion of two molecules of the former to one molecule of the latter, is reduced at a high temperature in a charcoal crucible.[2]

Detection and Estimation of Tungsten.

468 All the insoluble tungsten compounds can be converted into soluble tungstates by fusion, either alone with a caustic alkali, or with the addition of nitre. The solution when brought into contact with zinc and hydrochloric acid becomes blue-coloured, and when ammonium sulphide is added to the colourless solu-

[1] *Ann. Chem. Pharm.* lxxiii. 190 ; cv. 258.
[2] Wöhler, *Chem. Soc. Journ.* v. 94.

tion, and then dilute hydrochloric acid, a brown precipitate of tungsten sulphide is obtained, whereas hydrochloric acid alone precipitates tungstic acid, which on heating turns yellow. If the tungsten compounds are fused with a small quantity of tin in the reduction flame with microcosmic salt, a blue bead is obtained, whilst tungsten compounds containing iron yield in the reduction flame a blood-red bead.

Tungsten is determined *quantitatively* as the trioxide. For the purpose of determining the quantity contained in wolfram, for instance, the finely powdered mineral is heated with aqua regia, evaporated to dryness, the residue treated with water, the soluble chlorides of iron and manganese filtered off, and the insoluble tungstic acid washed with alcohol and dissolved in ammonia. The solution is then evaporated down, and the residue heated gently, and afterwards ignited in presence of air, when the trioxide remains, and is weighed.

The *atomic weight* of tungsten has been frequently determined with concordant results. Roscoe[1] obtained the number 183·33 by the reduction of the trioxide and re-oxidation of the metal, whilst the analysis of the hexchloride gave the number 183·59. Earlier estimations also gave numbers approaching 184, and hence the number 183·5 probably most nearly represents the truth.

URANIUM. U = 240.

469 The mineral known as pitchblende was formerly believed by certain chemists to be an ore of either zinc or iron, whilst by others it was thought to contain tungsten. Klaproth, in 1789, was the first to point out the existence in this mineral of a peculiar metal, to which he gave the name of uranium, in remembrance of Herschel's discovery of the planet Uranus, in the year 1781. The body obtained by Klaproth by the reduction of the calx of uranium was supposed by all the chemists who subsequently investigated the subject to be the metal, until Péligot[2] in 1842 proved this body to be an oxide. Péligot likewise isolated the metal and determined its atomic weight.

Uranium is not a very abundant element, and its chief ore is pitchblende. This consists of impure uranoso-uranic oxide, U_3O_8,

[1] *Mem. Man. Lit. and Phil. Soc.* [3] v. 77.
[2] *Ann. Chim. Phys.* [3], v. 5.

and is found in Cornwall, at Joachimsthal, Johanngeorgenstadt, Adrianople, and other localities. Uranium is also found as phosphate in uranite or uranium-mica, as carbonate in liebigite, whilst as urano-tantalite or samarskite it is found combined with niobium and tantalum. Pitchblende is the best source of uranium, this mineral usually containing from 40 to 90 per cent. of uranoso-uranic oxide U_3O_8. The following analysis by Ebelmen gives the composition of an average specimen of pitchblende:

Uranoso-uranic oxide, U_3O_8	75·23
Lead sulphide	4·82
Silica	3·48
Lime	5·24
Magnesia	2·07
Soda	2·05
Ferrous oxide	3·10
Manganous oxide	0·82
Carbon dioxide	3·32
Water	1·85
	101·98

The process recommended by Wöhler for the extraction of uranium from pitchblende is as follows: The powdered mineral is digested with sulphuric acid, small quantities of nitric acid being added from time to time to the mixture. As soon as the precipitate is transformed into a white powder and partially dissolved, the excess of sulphuric acid is driven off, and the residue digested with water. This leaves a residue of silica, lead sulphate, and the basic sulphates and arsenates of bismuth. The filtered liquid is then warmed, and a current of hydrogen sulphide passed through it, when arsenic, antimony, copper, and the rest of the lead and bismuth are thrown down. The filtrate is then oxidized by nitric acid, and an excess of ammonia added; the precipitate containing the ferric and uranic hydroxides is next washed with ammonia, and then digested at 100° with a concentrated solution of carbonate of ammonium containing an excess of ammonia. The uranic hydroxide dissolves, and the yellow double carbonate of uranium and ammonium crystallizes out on cooling. The mother-liquor still contains a small quantity of uranium, together with cobalt, nickel, and zinc, and these latter metals are precipitated by

sulphide of ammonium, which is added drop by drop until no further brown precipitate falls. The filtered liquid is boiled, and this soon deposits a yellow precipitate of ammonium uranate. Another process described by Péligot depends upon the facility with which uranic nitrate crystallizes, and upon its ready solubility in ether. Finely powdered pitchblende is treated with nitric acid, the acid solution evaporated to dryness, and the residue washed with water, leaving a residue consisting of sulphate of lead and ferric arsenates. The filtered liquid has a greenish-yellow colour, and yields on concentration a radiated crystalline mass. This is then dried, the mother-liquor evaporated, and the whole again crystallized. Long prismatic crystals are thus deposited, which must be washed with a small quantity of cold water, the washings being again used for dissolving another portion of the crude nitrate. After having been dried, the crystals are shaken up with ether, when uranium nitrate dissolves, and is obtained in the form of crystalline needles on evaporation of the ethereal solution.

470 *Preparation of Metallic Uranium.* Péligot first obtained uranium in the pure state, preparing it by the action of potassium or sodium on uranous chloride. A mixture of 75 grams of uranous chloride, UCl_4, 150 grams of dry potassium chloride, and 50 grams of sodium cut into pieces is placed in a crucible, and covered with potassium chloride. The crucible is then enclosed in a larger one, the space between them being packed with charcoal powder. The whole is slowly heated to redness in an air-furnace, and when the reaction has taken place the fire is strongly urged so that the metal fuses, but the flux does not volatilise. The reduced uranium is then found as a button inside a black very dense slag.

Uranium thus obtained has a specific gravity of 18·33. It is malleable and hard, and has a colour like that of nickel. It is permanent in the air at the ordinary temperature, and does not decompose water, but in the pulverulent state it takes fire at 207°, burning brightly, and forming the green oxide. It unites directly with chlorine with disengagement of heat and light, and combines with sulphur when heated together with it.

URANIUM AND OXYGEN.

471 Uranium forms two oxides, UO_2 and UO_3, and these combine to form intermediate oxides. The dioxide is a basic, whilst the trioxide is an acid-forming oxide, and both these are distinguished from other oxides by several remarkable properties. The dioxide combines directly with chlorine to form the compound UO_2Cl_2, which can also be prepared by dissolving the trioxide in hydrochloric acid. Other acids form with the trioxide corresponding compounds.

According to the suggestion of Péligot, the dioxide is usually regarded as a compound-radical, to which the name *uranyl* is given, the trioxide being the oxide of this radical. That the dioxide really acts as a compound-radical appears from an interesting observation made by Ebelmen[1] that the oxide precipitates metallic silver from its solutions without any evolution of oxygen.

Besides these, we are acquainted with other oxides containing less oxygen than the dioxide, and also with others which contain more than the trioxide; these compounds have, however, been but slightly investigated.

URANOUS COMPOUNDS.

472 *Uranium Dioxide*, UO_2. This oxide, formerly mistaken for the metal uranium, is obtained by heating the uranoso-uranic oxide or uranic oxalate in a current of hydrogen. Thus prepared it is a pyrophoric powder, having a brown or copper-red colour, and a specific gravity of 10·15. When heated in the air it takes fire, and is completely converted into the oxide, U_3O_8. It dissolves in strong acids, forming the green uranous salts.

Uranous Hydroxide is precipitated in reddish-brown flakes, which become black on ebullition, by adding an alkali to a uranous solution. It dissolves easily in dilute acids, whilst the calcined oxide is only difficultly soluble in these liquids.

Uranium Tetrachloride, or *Uranous Chloride*, UCl_4. This is produced with vivid incandescence, when chlorine is passed

[1] *Ann. Chim. Phys.* [3] v. 219.

over metallic uranium. It is also prepared by igniting uranous oxide in a current of dry hydrochloric acid. The best method of preparation is, however, to pass chlorine over an intimate mixture of charcoal and any of the oxides of uranium strongly heated in a tube of hard glass. It crystallizes in splendid dark-green regular octohedrons, having a metallic lustre, and volatilizing in red vapours. It is extremely deliquescent, fumes strongly on exposure to the air, and dissolves readily in water, with evolution of heat and formation of a deep emerald-green solution. This, when concentrated in a vacuum, leaves an amorphous deliquescent mass of uranous chloride, but when evaporated by heat it decomposes, yielding a soluble residue, probably consisting of the oxychloride. Solutions of uranous chloride yield with alkalis a precipitate of uranous hydrate. The solution acts as a powerful deoxidizing agent, reducing gold and silver salts, and converting ferric chloride into ferrous chloride.

It was by the analysis of this chloride that Péligot ascertained that the supposed metal was in reality an oxide. By reduction in hydrogen *Uranium sesquichloride*, U_2Cl_6, is obtained as a dark-brown powder.

Uranium tetrachloride combines directly with ammonia, forming the compound $3UCl_4 + 4NH_3$. This yields on heating a brown chloride, having the formula U_3Cl_8.

Uranium tetrabromide, UBr_4, is obtained by heating in an atmosphere of bromine vapour a previously ignited mixture of uranous oxide and six times its weight of starch. The bromide is deposited in the more strongly-heated portions of the tube as a brown powdery mass, exhibiting crystalline structure. It fumes in the air, and is very deliquescent.

Uranium Tetraiodide, UI_4, described by Rammelsberg, is the only known compound of uranium and iodine. It is obtained by dissolving uranous hydrate in hydriodic acid. A green solution is thus obtained, which decomposes on evaporation.

Uranium Tetrafluoride or *Uranous Fluoride*, UF_4, is obtained in the form of a voluminous green powder when hydrofluoric acid is added to a solution of uranous chloride. It is insoluble in water and hydrofluoric acid, and when heated in the air it leaves a green residue of oxide. When ignited in hydrogen it loses hydrofluoric acid, leaving a residue of the basic fluoride.[1]

Uranous fluoride forms double salts with the alkaline fluor-

[1] Carrington Bolton, *Berlin Acad. Ber.* 1866, 299.

ides. Potassium urano-fluoride, $KF.UF_4$, is obtained by the action of reducing agents, such as formic and oxalic acids, under the influence of light, upon potassium urano-oxyfluoride, described below. It is a green powder, resembling uranous fluoride, insoluble in water and in dilute acids.

Uranous Sulphate, $U(SO_4)_2 + 8H_2O$, crystallizes from aqueous solution in greenish rhombic prisms. In order to prepare this salt the green oxide, U_3O_8, is dissolved in dilute sulphuric acid, and the solution allowed to crystallize after addition of some alcohol. The mother-liquor, which contains uranyl sulphate, yields another crop of crystals of uranous sulphate, after it has remained exposed to the light, inasmuch as the uranyl present in solution is reduced by the alcohol, and uranous sulphate, being insoluble in dilute alcohol, separates out in crystals containing four molecules of water. Uranous sulphate forms double salts with the sulphates of the alkali-metals; as, for instance, $U(SO_4)_2 + K_2SO_4 + H_2O$, and $U(SO_4)_2 + (NH_4)_2SO_4 + H_2O$.

URANOSO-URANIC COMPOUNDS.

473 *Green Oxide of Uranium*, $U_3O_8 = UO_2 + 2UO_3$, occurs more or less pure in pitchblende. The pure oxide can be obtained by gently heating the trioxide or the dioxide in the air in the form of a satiny dark-green powder, having a specific gravity of 7·2, and soluble in strong acids.

Black Oxide of Uranium, or *Uranium Pentoxide*, $U_2O_5 = UO_2 + UO_3$, is formed when the other oxides, or ammonium uranate, are strongly ignited in the air. It is a black powder, used for painting on porcelain.

Uranium Pentachloride, UCl_5, is obtained by the direct union of the tetrachloride with chlorine. It exists in two distinct forms, according as it is produced slowly or quickly. When the current of chlorine is slow the pentachloride of uranium forms long dark needle-shaped crystals, which reflect light with a green metallic lustre, but are of a splendid ruby-red colour when viewed by transmitted light. If the rate at which the chlorine passes be rapid, the pentachloride is deposited in the form of a light brown mobile powder. The magnificent octohedral crystals of the tetrachloride are always deposited in quantity in that part of the tube nearest the heated mixture, then the black needle-shaped crystals of the pentachloride are

formed, mixed with more or less of the brown powder, which is generally carried a considerable distance along the tube. Both the black crystals and the brown powder are extremely hygroscopic, yielding yellowish-green liquids on exposure to the air for a few minutes, and hissing and giving off fumes of hydrochloric acid when thrown into water. Uranium pentachloride cannot be volatilized without partial decomposition, as when heated, either alone or in an atmosphere of chlorine, or carbon dioxide, uranium tetrachloride and free chlorine are formed. This dissociation begins in an atmosphere of carbon dioxide at 120°, and is complete at 235°, when the percentage of chlorine contained in the residue shows that one-fifth of the chlorine has been driven off. The tetrachloride when similarly heated loses no chlorine.[1]

URANIC COMPOUNDS.

474 *Uranic Oxide*, UO_3, or *Uranyl Oxide* $(UO_2)O$. When uranic nitrate, obtained by dissolving the lower oxides in nitric acid, is heated in a glass tube to 250° so long as acid fumes escape, this oxide is left behind in the form of a chamois brownish-yellow powder.

Uranic Hydrate, $UO_3 + 2H_2O$, cannot be obtained by precipitating a uranic salt by an alkali, the precipitate thus formed consisting of an alkaline uranate. It may, however, be prepared, according to Berzelius, by gently calcining the nitrate in a sand-bath as long as nitric acid is evolved. The residue contains uranic hydrate mixed with a basic salt, which can be removed by washing with boiling water. It may likewise be obtained by evaporating a solution of uranic nitrate in absolute alcohol, at a moderate heat, until a yellow mass remains, consisting of the hydroxide, $UO_2(OH)_2 + H_2O$. This hydrate loses half its water at 100°, or in a vacuum at the ordinary temperature, but at a temperature of 400° it begins to lose oxygen, and is converted into uranoso-uranic oxide. Uranic hydroxide is yellow, and has a specific gravity of 5·92. It does not undergo change in the air, nor does it absorb carbonic acid.

The uranyl salts are yellow-coloured, and most of them possess a remarkable power of fluorescence, which they impart to glass. The absorption bands exhibited by the uranyl compounds have been studied by Becquerel and others. These

[1] Roscoe, *Chem. Soc. Journ.* 1874, 933.

salts are also highly sensitive to light, and are frequently employed for photographic purposes.

Uranyl Chloride or *Uranium Oxychloride*, UO_2Cl_2, is formed when dry chlorine gas is passed over uranous oxide at a red heat. The tube then becomes filled with the orange-yellow vapour of this compound, which solidifies to a yellow crystalline mass, which is easily fusible, but not very volatile.

Uranyl chloride is soluble in water, alcohol, and ether, and its aqueous solution yields on evaporation crystals of the hydrate, $UO_2Cl_2 + H_2O$. This may be obtained in solution by acting upon uranic oxide with hydrochloric acid, or by oxidizing a solution of uranous chloride with nitric acid.

Uranyl chloride forms double chlorides with the chlorides of the alkali metals. The ammonium salt, $2NH_4Cl + UO_2Cl_2 + 2H_2O$, crystallizes in rhombohedrons from a syrupy solution of the mixed salts. The potassium salt, $2KCl + UO_2Cl_2 + 2H_2O$, is obtained by dissolving potassium uranate in excess of hydrochloric acid, adding chloride of potassium, and evaporating. Large rhombic tables separate out, which have a yellowish-green colour, and are very soluble. Uranyl chloride also combines with the hydrochlorides of the organic bases (Greville Williams).

Uranyl Bromide or *Uranium Oxybromide*, UO_2Br_2, is obtained by treating uranous oxide with bromine and water, or by dissolving uranic oxide in hydrobromic acid. On evaporation yellow needles are deposited, which have a styptic taste.

Uranyl Fluoride or *Uranium Oxyfluoride*, UO_2F_2, is obtained as a nearly white uncrystallizable mass, soluble in water and alcohol, by treating uranoso-uranic oxide or uranic hydrate with hydrofluoric acid and evaporating the solution (Berzelius; Bolton). It forms double salts with the alkaline fluorides.

Potassium Uranium Oxyfluoride, $UO_2F_2.3KF$, is a lemon-yellow crystalline precipitate, formed when an excess of potassium fluoride is added to a solution of uranyl acetate. It is purified by crystallizing from boiling water. Corresponding sodium, ammonium, and barium salts are known (Bolton).

475 *Uranyl Sulphate*, $UO_2SO_4 + 3H_2O$, is obtained by heating uranyl nitrate with sulphuric acid, and does not crystallize readily. When dissolved in moderately concentrated sulphuric acid, fine yellowish-green fluorescent crystals of $UO_2SO_4 + H_2SO_4$ are deposited on cooling, whilst from a solution in concentrated sulphuric acid crystals of a disulphate, $UO_2S_2O_7$, are

deposited, which do not fluoresce. By the gradual oxidation of the pitchblende found in Joachimsthal, several new uranium minerals have been formed. Amongst the more important are certain sulphates, such as uranium-vitriol or johannite, and some basic sulphates.

Uranyl sulphate forms double salts with the sulphates of the alkali metals, such as $UO_2SO_4 + K_2SO_4 + 2H_2O$. These are very soluble, and crystallize in yellow crusts, whilst the difficultly soluble ammonium salt, $UO_2SO_4 + (NH_4)_2SO_4 + 2H_2O$, is deposited in monoclinic lemon-coloured prisms.

Uranyl Nitrate, $UO_2(NO_3)_2 + 6H_2O$, is prepared by dissolving any of the oxides of uranium in nitric acid. It crystallizes in fine lemon-yellow fluorescent rhombic prisms, which are soluble in half their weight of water, and deliquesce on exposure.

Uranyl Phosphates. The normal orthophosphate is not known. When uranic oxide is treated with phosphoric acid, a crystalline powder is obtained which is partially soluble in water, and the solution deposits yellow crystals of the di-hydrogen salt, $UO_2(H_2PO_4)_2 + 3H_2O$. The residue contains $2UO_2(H_2PO_4)_2 + 3H_2O$.

Uranyl Ammonium Phosphate, $UO_2NH_4PO_4$, is a greenish-yellow precipitate, insoluble in acetic acid, obtained by adding a soluble phosphate to a solution of uranyl acetate containing sal-ammoniac. This reaction is employed for the volumetric determination of uranium as well as for that of phosphoric acid.

Several double phosphates occur as minerals; thus $(UO_2)_2Ca(PO_4)_2 + 8H_2O$, is known as uranochalcite.

Uranyl Arsenates. Several of these compounds exist as minerals (Winkler). Trögerite has the composition $(UO_2)_3(AsO_4)_2 + 12H_2O$; walpurgine is a basic arsenate of uranyl and bismuth; uranospinite is an arsenate of uranium and calcium.

Uranyl Carbonates. Double salts of uranyl carbonate and alkaline carbonates are obtained by precipitating a uranyl salt with an alkaline carbonate. The potassium salt, $UO_2CO_3 + 2K_2CO_3$, is obtained by dissolving potassium uranate in bicarbonate of potash, and evaporating at a moderate temperature, when the compound deposits in silky crystalline crusts. Water dissolves at the ordinary temperature seven per cent. of its weight of this salt. The corresponding sodium salt is obtained in a similar way, and possesses corresponding properties. The ammonium compound, $UO_2CO_3 + 2(NH_4)_2CO_3$, is prepared by gently warming ammonium uranate with a solution of ammonium

carbonate. The salt separates out on cooling in lemon-yellow small flat monoclinic prisms. It dissolves at the ordinary temperature in 20 per cent. of water, but is less soluble in water containing carbonate of ammonia. The mineral liebigite is an apple-green warty mass, occurring together with other uranium minerals. It is a uranyl calcium carbonate, $UO_2CO_3 + CaCO_3 + 10H_2O$.

THE URANATES.

476 Uranyl oxide not only forms the uranyl salts, but also unites with basic metallic oxides to form the *uranates*. The alkaline uranates are obtained by precipitating a uranic salt with an alkali, those of the alkaline earths and other metals by precipitating a mixture of a uranic salt and a corresponding metallic salt with ammonia. They are also formed when a mixture of metallic uranate and the acetate or carbonate of the metal is heated in the air. The uranates generally have the composition $M_2O.2UO_3$, and correspond to the dichromates. They are yellow, insoluble in water but soluble in acids, and are decomposed by heat, like uranic oxide itself.

Potassium Uranate, $K_2U_2O_7$. This is obtained as a pale orange-yellow coloured powder by precipitating a uranic salt with an excess of potash, or by fusing uranic oxide with potassium carbonate.

Sodium Uranate, $Na_2U_2O_7$, is obtained like the potassium salt, and is known as uranium yellow, being used for painting on glass and porcelain, as well as for preparing the yellow glass known as uranium glass. It is prepared on the large scale by roasting 100 parts of pitchblende, containing 45 per cent. of U_3O_8, with 14 parts of lime in a reverberatory furnace. The resulting calcium uranate is treated with dilute sulphuric acid, and the solution of uranic sulphate thus obtained is mixed with sodium carbonate. The uranium is precipitated together with the other metals, but re-dissolves in an excess of the alkali. On treating this liquid with dilute sulphuric acid, a hydrated sodium uranate, or uranium yellow, $Na_2U_2O_7 + 6H_2O$, is obtained.[1]

Ammonium Uranate. This salt sometimes occurs in commerce as a fine deep yellow-coloured precipitate, termed, like the sodium salt, uranium yellow. It is easily obtained by adding

[1] Patera, *Journ. Pract. Chem.* lxi. 397.

ammonium chloride or sulphate to a boiling solution of sodium uranate, washing the resulting precipitate, and drying at a gentle heat. When heated to redness this salt yields pure uranoso-uranic oxide, and serves therefore as the raw material for the preparation of other uranium compounds.

URANIUM TETROXIDE AND THE PERURANATES.

477 These compounds were discovered by Fairley,[1] but have not yet been thoroughly examined.

Uranium Tetroxide, UO_4. When a very dilute solution of hydrogen dioxide is added to one of uranyl nitrate, a yellowish-white precipitate of UO_4+2H_2O is formed, which evolves chlorine when treated with hydrochloric acid. If uranyl nitrate solution be added to a mixture of hydrogen dioxide and a large excess of sulphuric acid, no precipitate is obtained, but on standing for some time a small quantity of the anhydrous oxide separates out as a heavy, colourless crystalline powder.

Potassium Peruranate, $K_4UO_8 + 10H_2O$, is a yellow or orange precipitate formed when alcohol is added to a solution of uranyl nitrate, caustic potash, and hydrogen dioxide. The salt is very unstable, losing oxygen, and rapidly absorbing carbon dioxide on exposure.

Sodium Peruranate, $Na_4UO_8 + 8H_2O$, is formed in a similar manner to the preceding compound, and crystallizes in golden-yellow needle-shaped crystals, which are somewhat more stable than the potassium salt. If the minimum quantity of caustic soda be employed, a red crystalline salt separates out, having the composition $Na_2U_2O_{10} + 6H_2O$. This may be regarded as uranyl sodium peruranate $(UO_2)Na_2UO_8 + 6H_2O$, and, in the same way, the tetroxide may be considered to be uranyl peruranate $(UO_2)_2UO_8$.

URANIUM AND SULPHUR.

478 *Uranous Sulphide*, US_2, is obtained, according to Péligot, when metallic uranium is heated in sulphur vapour. The mass takes fire and an amorphous greyish-black powder is obtained

[1] *Chem. Soc. Journ.* 1877, i. 127.

which becomes crystalline when ignited in absence of air. It may also be formed by the action of sulphuretted hydrogen on uranium tetrachloride heated to redness. Sulphide of ammonium also gives a black precipitate of the hydrated sulphide with uranium salts. When exposed to moist air the sulphide gives off hydrogen sulphide and is converted into uranyl sulphide, UO_2S.

Uranyl Sulphide, UO_2S, is precipitated when sulphide of ammonium is added to a solution of uranic nitrate. It dissolves partially in cold water, forming a brown solution.

Uranic sulphide has not been obtained, but double salts exist of this sulphide with sulphides of potassium and ammonium. Thus if the precipitate formed by sulphide of ammonium in a uranic salt be left for a short time in contact with the liquid the whole is converted into a blood-red compound containing sulphide of ammonium, and this when treated with caustic potash solution yields a red powder termed uranium-red. Its composition is very complex, and its constitution is doubtful. The red uranium compound yields corresponding red compounds with sodium, barium, and strontium.[1]

Detection and Estimation of Uranium.

479 The most characteristic reactions of uranium have been already described.

The uranous salts are green, and pass rapidly by oxidation into the uranyl-salts which are precipitated yellow by alkalis and their carbonates. In the general separation of the metals uranium is obtained together with iron. In order to separate these, the precipitated oxides are washed and treated with a concentrated solution of carbonate of ammonium, and filtered. Uranium is detected in the filtrate after supersaturation with hydrochloric acid, by the brown precipitate produced with ferrocyanide of potassium. When a uranium compound is fused with microcosmic salt in the oxidizing flame, a yellow bead is obtained which on cooling becomes green, and on re-heating attains a darker green colour. The uranyl salts yield a peculiar absorption spectrum which has been described by Morton and Bolton.[2]

In order to determine uranium *quantitatively*, it is converted

[1] Patera, *Ann. Chem. Pharm.* lxxxvi. 254; Remele, *Journ. Pract. Chem.* xcvii. 193.

[2] *American Chemist*, iii. 360 and 401.

into the uranyl salt, precipitated with ammonia, and the washed precipitate converted by oxidation into the green oxide. It may then, like iron, be determined volumetrically with a solution of potassium permanganate, having previously reduced the uranyl compound in presence of zinc and sulphuric acid into uranous salt, or the solution of uranyl acetate may be precipitated by sodium phosphate.

The uranium compounds do not impart any tint to the non-luminous gas-flame. The spark-spectrum of uranium is a complicated one, and has been mapped by Thalén. It consists of a large number of lines of which a series of five in the green are conspicuous by their brightness, viz., w.l. 5493, 5481, 5479, 5477, and 5474; also three specially bright in the more refrangible portions, viz., 4472, 4362, and 4340.

The *atomic weight* of uranium was determined by Péligot by the analysis of the tetrachloride which he found to contain 37·2 per cent. of chlorine, whence he calculated the number 238·8 as the atomic weight. He afterwards obtained the number 239·5 by the conversion of the acetate, $UO_2(C_2H_3O_2)_2+H_2O$, into the dioxide. These numbers agree with the observations of other chemists so nearly that, as no other exact determinations have been made, the atomic weight is usually assumed to be 240.

Position of Uranium amongst the Elements. Until recently uranium was classed in the iron group of metals and considered to possess the atomic weight 120, its oxides corresponding to those of iron and having the formulæ UO and U_2O_3. As, however, the highest oxide of uranium, like the highest oxides of the other metals of the chromium group, is a distinctly acid-forming oxide, and as uranium yields uranyl compounds analogous to chromyl compounds, and, moreover, as uranium, like molybdenum and tungsten, combines with five atoms of chlorine to form a pentachloride, uranium is now usually classed with chromium, and supposed to have an atomic weight of 240. The positive solution of the question of the position of uranium amongst the elements can, however, only be decided by a vapour-density determination of a volatile chloride or bromide or by a specific-heat determination of the metal.

METALS OF THE TIN GROUP.

Tin.	Zirconium.
Titanium.	Thorium.

THESE metals are closely connected with the non-metallic element silicon, inasmuch as they form dioxides corresponding to SiO_2, as well as volatile tetrachlorides like $SiCl_4$. Their fluorides, moreover, combine with the fluorides of other metals to form salts corresponding to, and isomorphous with, the silico-fluorides.

TIN (Stannum), Sn = 117·8.

480 This metal was known in early times. It is very uncertain whether the word "bedil" in the Old Testament, which is translated by the Greek word *κασσίτερος*, and by the Latin *stannum*, was originally used to designate tin. It is likewise doubtful whether the metal which the Phœnicians are said to have brought from the Cassiterides, whose exact locality was unknown to Herodotus, was really tin. Possibly the Greek word is connected with the Arabic "kasdir," which signifies tin. It is, however, certain that at the beginning of our era the word was used to specify tin, for Pliny states that *cassiteron* and *plumbum candidum* are the same, and he adds that it is more expensive than *plumbum nigrum* (lead); he moreover states that it serves for soldering the latter metal, and that it is obtained from the Cassiterides in the Atlantic Ocean. That the Cassiterides really were the British Islands appears more than probable, for after Cæsar's conquest tin was carried from the Cornish mines through Gaul, by way of Marseilles to Italy;[1] and Diodorus

[1] G. Smith, *The Cassiterides*. London, 1863.

Siculus mentions that the inhabitants carry the tin to a certain island called Iktis, lying on the coast of Britain. "During low water the intermediate space is left dry, and they then carry over abundance of tin to this place in their carts." There can be little doubt that the Iktis of Diodorus is St. Michael's Mount, in Mount's Bay, in Cornwall; for up to the present day a causeway exists, flooded at high water, but dry at low water, across which the inhabitants are in the habit of carrying goods to and from the mainland. The names by which Pliny designates tin and lead seem, however, to show that he did not consider these as distinct metals, but rather as varieties of one metal, and he adds, "Sequitur naturæ plumbi cujus duo genera, nigrum atque candidum." The word *stannum*, which at a later period became the general designation for tin, also occurs in Pliny's works, though it appears certain that by this word he did not signify tin, but rather any mixture of metals which contains lead. Geber was well acquainted with tin, and he mentions its most important properties, especially that peculiar crackling sound which the metal emits when bent, as well as the fact that it forms brittle alloys. Tin was termed *Jupiter* by the alchemists, and to it the sign ♃ was given; but owing to the above-mentioned property of forming brittle alloys it was some times termed, by them, *diabolus metallorum*.

Tin has been found in small quantities in Siberia, Guiana, and Bolivia in the native state, together with metallic gold, though the metallic tin from the last-named locality may, according to Forbes,[1] possibly have been an artificial product.[2] It has also been found in small tablets in bismutite from Mexico.

The chief ore of tin is cassiterite, or tinstone, a more or less pure form of the dioxide, SnO_2. Less frequently it is found as tin-pyrites, $Cu_4SnS_4 + (FeZn)_2SnS_4$, and occasionally as silicate. It also occurs in small quantity in certain epidotes, as well as in columbites, tantalites, and other similar minerals. Various mineral-waters likewise contain traces of tin, and this metal has also been detected in certain meteoric masses.

481 *The Metallurgy of Tin.* All commercial tin is obtained from tinstone, which is found in veins traversing the older crystalline and schistose rocks. The same is also found as *stream-tin* in water-worn nodules amongst the detritus of the same rocks.

[1] *Phil. Mag.* [4], xxix. 133; xxx. 142.

[2] We have examined the specimen of metallic tin described by Forbes, and are inclined to believe it to be a natural product.

Tin ore is not, however, very widely distributed, only occurring in large masses in a few localities. The oldest and best known tin mines from which tin has continuously been obtained probably from the time of the Phœnicians up to the present, are those of Cornwall. The ore there occurs in the granite and in the metamorphic schistose rock, and is found especially rich in the killas, a metamorphic clay state, and in the line of junction of this with granite. It is found in veins or lodes, in beds or flats, and in ramifications of small veins or "stock werke," and these tin veins usually run in Cornwall in an easterly or westerly direction. The following minerals are frequently found, together with tinstone: wolfram, apatite, topaz, mica, tourmaline, arsenical pyrites, &c.

Tin mines exist, although on a much smaller scale than in Cornwall, in other parts of Europe, as in the Erzgebirge, in Bretagne, and in the Spanish province of Galicia. Very large deposits of tin ores are, however, found in other quarters of the globe. Thus, for instance, in the Island of Banca, and on the Malay Peninsula, large quantities of tin-ore are found, chiefly in the form of stream-tin, though it likewise occurs in lodes in granite rocks. This source of tin was discovered at the beginning of last century, and at a later time very rich mines, which are now worked, were discovered in the neighbouring Islands of Bilitong. Tin has also been worked in Bolivia and Peru, and lately very large quantities of tin have been obtained from Australia, and especially from New South Wales and Queensland. In New South Wales the production of tin rose from 47 tons in 1872 to 60,58 tons in 1875,[1] whilst in Queensland a similarly rapid progress has been made. The effect of these discoveries of Australian tin-ore has been to depress, or rather almost to extinguish, Cornish tin-mining.

The process adopted in Cornwall for the reduction of the metal is a simple one. The ore, which consists not only of Cornish stone, but likewise of Australian and Peruvian ore, after being stamped, is washed to free it as much as possible from gangue, and is then roasted in calcining furnaces for the purpose of driving off the sulphur and arsenic contained in the arsenical and ordinary pyrites generally mixed with the ore. The vapours from these revolving calcining furnaces are led into chambers in which the arsenic trioxide condenses. The construction of an Oxland and Hocking's revolving calciner

[1] *The Industry of New South Wales*, G. H. Reid. Trübner, 1878.

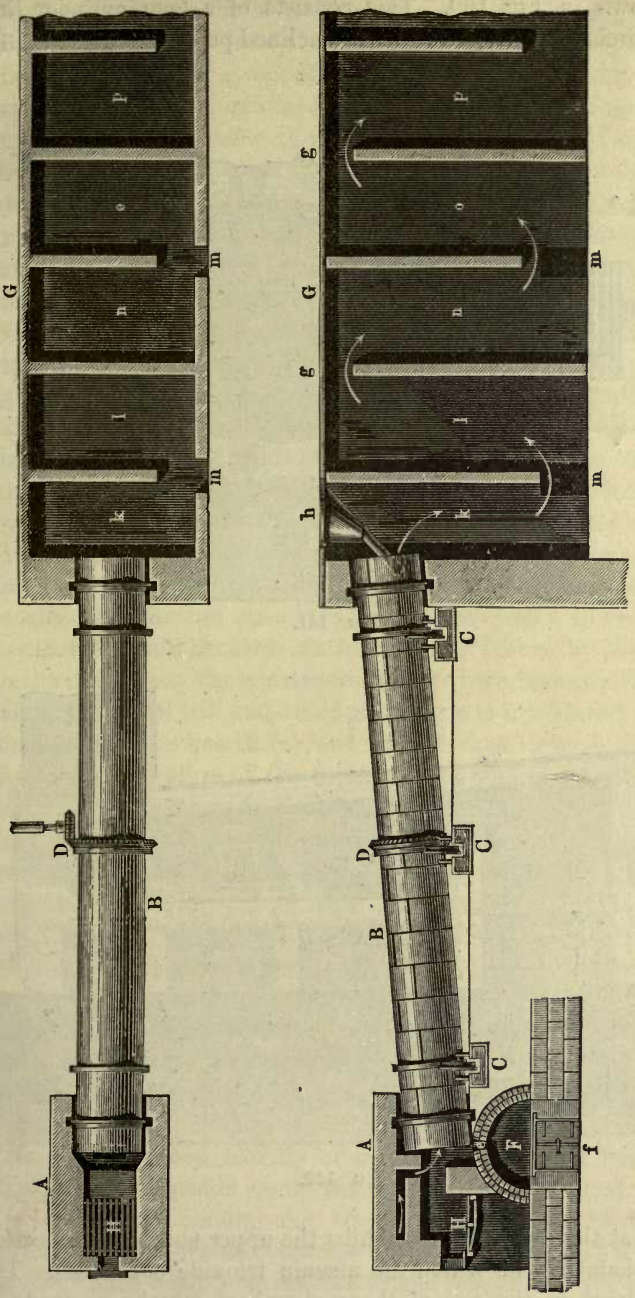

FIG. 160.

is shown in Fig. 160. This consists of a long cylinder lined with firebrick, and placed in an inclined position. The fire (H) is

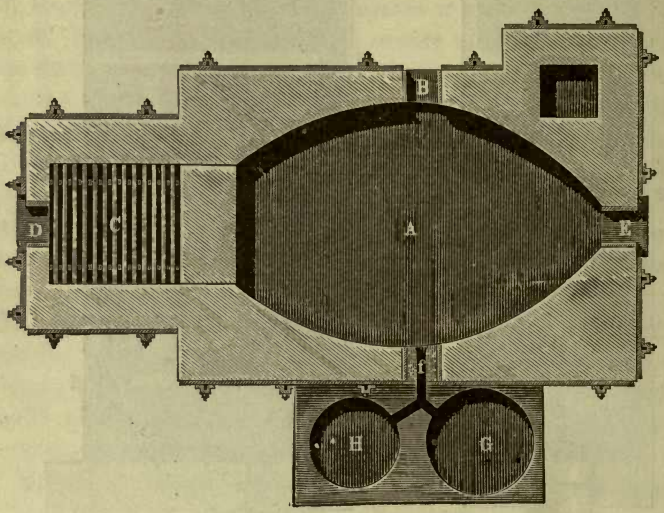

Fig. 161.

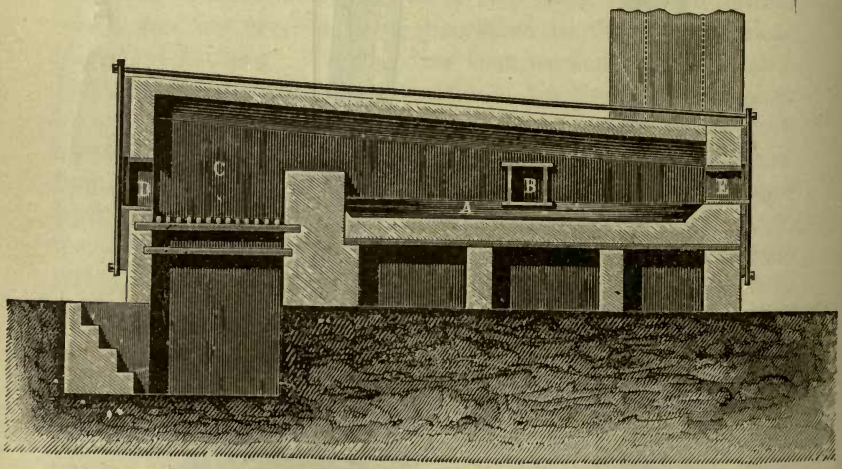

Fig. 162.

placed at the lower end (A), whilst the upper end is in connection with chambers in which the arsenic trioxide condenses. The ore is dried on the top of these chambers, which are made of

iron plate, and then brought by means of the hopper (h) into the cylinder, and the roasted ore falls down into the space (F). This then undergoes a second washing in order to remove the ferric oxide and other oxidized materials, and is again roasted for the purpose of volatilizing the last traces of arsenic and sulphur. After these operations the roasted ore is found to contain from 60 to 70 per cent. of tin. It sometimes happens that the tin ore is mixed with more or less wolfram, $(FeMn)WO_4$, and as this mineral possesses a high specific gravity, it cannot be removed from the tin ore by washing. In order to remove this impurity, the presence of which in the smelting operations would prove injurious to the quality of the tin obtained, the following process proposed by Oxland is generally adopted. The roasted ore is smelted in a reverberatory furnace with a sufficient quantity of soda-ash to furnish a soluble tungstate of the alkali, toegther with the oxides of iron and manganese. The soluble tungstate is next removed, by solution in water, from the oxides of iron and manganese, and the unaltered tinstone. The roasted ore, or *black tin*, is then mixed with one-fifth part its weight of anthracite and the mixture sprinkled with some water in order to prevent the finely divided ore from being blown by the draft into the chimney. The construction of the reverberatory furnace is shown in Figs. 161 and 162; the charge is introduced by the door (B) on to the hearth (A), and then worked through the door (E). The temperature of the furnace is gradually raised for five hours, the charge then repeatedly stirred, and at the expiration of six hours the reduced metal is tapped and allowed to run from the lower part of the hearth through the hole (f) into the vessel (G). The impure tin thus obtained is then cast into moulds, and these are refined by the process of *liquation*. This is effected by placing the ingots in another similar reverberatory furnace which is gradually heated, so that the pure, more easily fusible tin first melts and runs into a cast-iron vessel (H) placed below, whilst the less fusible alloy of tin with iron and arsenic remains on the hearth. A fire is placed under the vessel (H) in order to keep the metal liquid, and this is then stirred up with a pole of green wood, usually of an apple-tree. The length of this operation depends upon the quality of the metal which it is desired to obtain, and may last from one to several hours. The dross which separates during the process of refining, and the "hard-head," or residue which remains on the hearth, both of which contain large quantities of tin, are afterwards

worked up. In order to prepare *grain-tin* the block tin is heated until the metal becomes brittle and crystalline; it is then broken up by a hammer, or allowed to fall from a considerable height.

Of the various sorts of commercial tin that from Banca is the purest. It contains only traces of copper, lead, and iron; and for this reason it is usually employed by chemists and manufacturers as the source of the tin salts. Next in order of purity comes English tin. The impurities contained in the common commercial varieties of tin are arsenic, antimony, bismuth, zinc, lead, copper, iron, and less frequently molybdenum, tungsten, and manganese.

482 *Properties and uses of Tin.* Tin is a white, brightly lustrous metal, which melts at 235°, volatilizes at a white heat, and, according to the experiments of Matthiessen, has a specific gravity at 13° of 7·293. It is harder than lead, but softer than gold. It exhibits a fibrous fracture, and when bent emits a peculiar crackling sound, caused by the friction of the crystalline particles. Tin can be easily rolled or hammered out to thin foil, and at a temperature of 100° it may be drawn into wire, which, however, possesses but slight tenacity; but at 200° it becomes so brittle that it may be powdered. A sample of Banca tin which was exposed at St. Petersburg to a very low temperature during the winter, fell to granular crystalline pieces, or to a coarse powder. This alteration of structure may be artificially produced by lowering the temperature of the metal to the freezing point of mercury.[1] If zinc be brought into a solution of tin chloride the metal separates out in the form of fine crystalline dendrites, and this deposit, known as the tin-tree (Arbor Jovis), was first prepared by Ilsemann in 1786. When tin is melted and then allowed partially to solidify, the liquid portion being poured off, needle-shaped prismatic or tabular crystals of the metal remain behind. Another mode of obtaining crystalline tin is to decompose tin chloride by a weak galvanic current when the metal is deposited in quadratic prisms and pyramids. Fine crystals of tin can also be obtained when water containing zinc dust in suspension is gradually added to a solution of tin chloride.

Tin is used for a large number of purposes, for the preparation of vessels for household and technical use, for the manufacture of tin-foil, for tinning copper and iron, and especially for preparing the alloys of tin. Tinned copper vessels were

[1] Fritzsche, *Ber. Deutsch. Chem. Ges.* ii. 112, 540.

employed by the ancients, for we find them described by Pliny; and the same author also mentions as a well-known fact, that in the process of tinning, the weight of copper articles increases but slightly, and he adds that the substance termed stannum was employed for this purpose.

Copper- and brass-ware can readily be tinned by dipping the vessel into the molten metal. In order to cover the interior of a vessel with a coating of tin, it is heated and some molten tin poured in, which is then well divided over the surface by rubbing with rags. In order to prevent the oxidation of the metal a small quantity of resin or sal-ammoniac is added. Agricola was the first to mention the process of tinning iron. It appears, however, that at that time it was only slightly employed. The process is usually supposed to have been discovered in Bohemia in 1620, coming into use in England and France about 100 years later. For the purpose of preparing the common tin plate the iron plate is dipped into hydrochloric acid or dilute sulphuric acid, then rubbed over with sand and water, and lastly dipped into a bath of hot fat, in order to dry and warm it. From this it is brought into a vessel filled with melted tin covered with a film of oil, an alloy of tin and iron being thus formed. This is covered with a film of pure tin by dipping it into a second bath of the metal, and the sheets are lastly dipped into heated tallow in order to remove the excess of tin.

ALLOYS OF TIN.

483 Several of these alloys are largely employed in the arts. Tin and lead may be mixed in any proportion, and the alloy, termed pewter, is harder and tougher, but more readily fusible than either of the two metals. For this reason it is employed as a solder. The following table gives the composition of some of the different lead and tin alloys:

	Common Pewter.	Solder.		
		Fine.	Common.	Coarse.
Tin . .	4	2	1	1
Lead . .	1	1	1	2

Although the alloys of tin and copper possess a great commercial importance, these metals do not readily unite with one

another, and the compound produced is not a stable one; hence the mass seldom remains perfectly homogeneous, though more so than the silver copper alloys. The effect of heat on the copper-tin alloys is remarkable, for whilst steel becomes harder by tempering, these lose their brittleness, and become malleable if they are heated and then plunged into cold water. The most important of these alloys are:—

Gun-metal usually contains nine parts of copper to one of tin, and has a yellow colour. This alloy also serves for the preparation of bronze medals.

Speculum-metal is composed of one part of tin to two parts of copper, melted together, with, frequently, addition of a small quantity of arsenic. It possesses a steel-grey colour, is very brittle, and takes a very high polish.

Bell-metal possesses a varying composition. It generally consists of from 4 to 5 parts of copper to 1 of tin. It has a yellowish-grey colour, and readily melts to form a thin liquid. It has a finely granular structure, is hard, brittle, and very sonorous. The Chinese gongs and tom-toms are cast at a very high temperature, and then quickly brought under the hammer, in consequence of which treatment the alloy becomes very dense.

Bronze. True bronze consists of copper, tin, and sometimes a small quantity of lead. The other metals which are found are impurities, but modern bronze always contains zinc. The colour of bronze is a more or less reddish-yellow. It is hard and tough, and may be filed and worked in the lathe, whilst in its molten state it forms a mobile liquid.

The table on the next page gives the composition of some of the above described alloys.

Phosphor-bronze. The addition of phosphorus to bronze imparts to it a character of greater hardness, elasticity, and toughness. This material is obtained by melting copper with tin-phosphide with sometimes a small addition of lead. It contains from 0·25 to 2·5 per cent. of phosphorus, and from 5 to 15 per cent. of tin, and is largely used, especially that containing from 7 to 8 per cent. of tin for portions of machinery for which hardness and toughness are important properties. The alloy containing more tin has been employed for bell-metal. Its valuable properties are connected with the fact that copper forms a homogeneous alloy, with tin phosphide, the presence of phosphorus preventing the oxides from dissolving and thus impairing the qualities of the metal.

Analyses of Alloys of Tin.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
Cu .	91·74	67	73·94	82	84·25	87·89	84·53	85·9	70·30	89·43	89·78	88·77	89·34	84·20
Sn .	8·26	30	21·67	17	15·64	10·58	6·82	14·1	24·53	8·17	9·16	9·25	7·50	3·05
Pb .	—	—	1·19	—	—	—	8·65	—	5·20	1·05	1·33	0·71	1·21	0·75
Fe .	—	—	0·17	1	trace	0·27	—	—	—	0·34	—	—	—	—
Zn .	—	—	—	—	—	—	—	—	—	—	2·35	1·28	1·61	11·55
Ni .	—	—	2·11	trace	—	—	—	—	—	0·19	—	—	—	—

I. English gun-metal.
II. Speculum metal used in construction of Lord Rosse's large telescope.
III. Bell cast in 1670 in Darmstadt.
IV. Chinese gong.
V. Egyptian bronze coin of the reign of Ptolemy IX.
VI. Attic bronze coin.
VII. Roman bronze coin of Justinian.
VIII. Gaulish axe.
IX. Celtic arrow-head.
X. Bronze statue of sixteenth century from Augsburg.
XI. Statue of Germanicus, cast in Berlin in 1824.
XII. Thorwaldsen's Shepherd, cast in Berlin in 1825.
XIII. Statue of Bacchus in Berlin, 1830.
XIV. Statue of Lessing in Brunswick.

484 *Tin Amalgam.* Tin readily combines with mercury with diminution of temperature. The amalgam may be formed more quickly when mercury is poured into molten tin, and, according to the quantity of the mercury added, the amalgam is either liquid, or forms a granular or crystalline mass. When mercury is made the negative pole in a solution of tin dichloride, fine crystals of the amalgam are obtained containing from 44 to 51 per cent. of tin (Joule). Tin amalgam is largely used for silvering mirrors. For this purpose tin-foil, which usually contains from 1 to 2 per cent. of copper and a small quantity of lead, is spread out on a perfectly even horizontal slate table. This is then covered with a film of mercury from about 2 to 3 mm. in thickness, and the carefully cleaned sheet of plate glass floated on to its surface, the excess of mercury being pushed forward and thus the formation of bubbles of air guarded against. The glass is then gradually weighted evenly throughout its surface in order to remove the excess of mercury. After the lapse of some time the weights are removed and the plate gradually inclined in order that the excess of liquid amalgam may flow away.

It is not certain when this process for manufacturing mirrors was first employed, inasmuch as, during the middle ages, the processes used in the preparation of mirrors were kept secret. It is, however, clear that before amalgam was used, a surface of metallic lead was employed for obtaining a mirror as early as the thirteenth century, when such mirrors were common. These were curved, and were prepared, as Beckmann describes in his *History of Inventions*, from large glass globes, into the interior of which a mixture of resin, molten lead, and sulphide of antimony was introduced, the fluid mass being brought over the surface until it was all covered with a thin film. The globe was then cut into pieces, and the mirrors thus obtained were often employed as ornaments. A guild of glass-mirror makers existed at Nürnberg in the year 1373 ; whether they made mirrors according to the above process is doubtful, but these, as well as French workmen, sold products of their art in the Venetian market up to the year 1500. The use of amalgam for coating mirrors is first mentioned by Kunkel, who recommends for the purpose an amalgam of 2 parts of quicksilver 1 of marcasite (bismuth), $\frac{1}{2}$ part of tin, and $\frac{1}{2}$ part of lead.

TIN AND OXYGEN.

485 The fact that tin readily forms a calx was observed at an early period. Pelletier was the first, in the year 1792, to show that tin combines in two proportions with oxygen, forming two series of salts. This investigation was continued by Proust, but for a long time considerable doubt existed as to the number of the oxidation products of the metal. Berzelius in 1812 assumed that there were three oxides, SnO, Sn_2O_3, and SnO_2, on the grounds that when the metal is oxidized by nitric acid the highest oxide thus prepared possesses a totally different chemical character from that which is obtained by precipitation with alkalis from a solution of the salts of tin. The subsequent investigations of Davy, Gay-Lussac, and Berzelius himself, proved that only the first and last of these oxides exist.

Tin monoxide or stannous oxide is a base; the dioxide or stannic oxide acts both as a basic and as an acid-forming oxide. Their compounds are distinguished as the stannous and stannic salts.

STANNOUS COMPOUNDS.

486 *Tin Monoxide* or *Stannous Oxide*, SnO. This oxide may be prepared in a variety of ways. In the first place it is obtained as an olive-coloured powder when stannous oxalate is ignited out of contact with air. Secondly it may be prepared by adding a solution of potassium carbonate to one of tin dichloride, when a white precipitate, having the composition $Sn_2O_3H_2 = 2SnO + H_2O$, is thrown down. This readily absorbs oxygen from the air, but if it be washed in absence of air and dried in a stream of carbon dioxide, the monoxide remains behind as a black powder. Stannous oxide is also obtained when the pure dichloride is mixed with crystalline carbonate of soda, the mass heated until it has become black, and then lixiviated. If the hydrated oxide be boiled with caustic soda the anhydrous oxide is obtained as a crystalline powder consisting of cubes modified with the faces of the dodecahedron. It may also be obtained in the crystalline state by digesting a nearly saturated solution of the hydrated oxide in acetic acid at a temperature of 56°.

Stannous oxide readily takes fire when heated in the air, and turns black on exposure to sun-light. The stannous salts are obtained by dissolving tin in acids. They possess an unpleasant metallic taste, redden litmus, and readily absorb oxygen, and hence serve as powerful reducing agents.

Tin Dichloride or *Stannous Chloride*, $SnCl_2$, is obtained on the large scale by dissolving tin in hydrochloric acid. On evaporating the solution and cooling, crystals of hydrated stannous chloride, $SnCl_2 + 2H_2O$, known in commerce as *Tin Salt*, separate out in transparent monoclinic prisms which melt in their water of crystallization at 40°, and on cooling again yield a crystalline mass. They have a specific gravity of 2·71, and dissolve at the ordinary temperature in 0·37 parts of water. When more strongly heated they partially decompose with evolution of hydrochloric acid, but when dried in vacuum over sulphuric acid they lose their water. The anhydrous salt, which may also be obtained by heating tin in hydrochloric acid gas, or together with corrosive sublimate, is a transparent mass having a fatty lustre and conchoidal fracture. It fuses at 250° to form an oily liquid which boils a little below a red-heat with partial decomposition. The hydrated salt dissolves in a small quantity of water with diminution of temperature forming a clear liquid which when diluted with much water becomes turbid, a basic chloride, $2Sn(OH)Cl + H_2O$, being precipitated, and this again dissolves on the addition of acids. The same precipitate is formed when the clear solution is exposed to the action of the air:

$$3SnCl_2 + H_2O + O = SnCl_4 + 2Sn(OH)Cl.$$

Stannous chloride also dissolves in alcohol and forms easily soluble double salts with the chlorides of the alkali-metals.

Tin Dibromide or *Stannous Bromide*, $SnBr_2$, is obtained when tin is heated in hydrobromic acid gas or distilled with mercuric bromide. It forms a grayish-white easily fusible crystalline mass soluble in water. A solution of this compound is obtained by acting with hot aqueous hydrobromic acid upon metallic tin.

Tin Di-iodide or *Stannous Iodide*, SnI_2, is best obtained by adding a small excess of iodide of potassium to a warm concentrated solution of stannous chloride. It crystallizes in yellowish-red needles which dissolve only slightly in water, though readily in warm solutions of the chlorides and iodides of the alkali-metals, and also in dilute hydrochloric acid. It melts under a red-

heat solidifying to a crystalline mass which liquefies at a higher temperature. When heated in absence of air it is obtained in the form of a red crystalline mass yielding a scarlet powder.

Tin Difluoride or *Stannous Fluoride*, SnF_2, is obtained by dissolving the hydrated monoxide in hydrofluoric acid. On evaporation in absence of air this compound is obtained in the form of small white monoclinic tables.

The bromide, iodide, and fluoride combine, like the chloride, with the corresponding haloid compounds of the alkali-metals and with those of the metals of the alkaline earths to form crystalline double salts.

Stannous Sulphate, $SnSO_4$, is formed by dissolving the metal or the hydrated oxide in dilute sulphuric acid. On evaporation in a vacuum microscopic granular crystals are obtained which are only a little more soluble in hot than in cold water. The solution readily deposits a basic salt.

Stannous Nitrate, $Sn(NO_3)_2$. This salt is only known in solution, obtained by the action of very dilute nitric acid on the hydroxide or on the metal, in the latter case ammonium nitrate being simultaneously produced:

$$4Sn + 10HNO_3 = 4\,Sn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

The yellow solution quickly becomes turbid on exposure to the air.

STANNIC COMPOUNDS.

487 *Tin Dioxide* or *Stannic Oxide*, SnO_2, occurs in nature as tinstone or cassiterite crystallizing in the quadratic system (Fig. 163) and possessing an adamantine lustre. The crystals are seldom colourless, being generally tinted of a brown or black colour from the presence of the oxides of manganese and iron. *Stream-tin* is found in water-worn nodules, and *Wood-tin* in reniform fibrous masses. When tin is heated nearly to its boiling-point in the air, it burns with a luminous white flame, and the dioxide which is thus formed in a state of fine division was formerly known as *flores jovis*. If fused in the presence of air, the surface of the metal soon becomes covered with a gray pellicle, which then passes into a gray powder known as *flores stanni*, and this consists of a mixture of finely-divided metal with the oxide which, on continuous ignition, is wholly

converted into stannic oxide. The dioxide is also obtained on treating tin with nitric acid, when a violent oxidation occurs. The hydrated white powder thus obtained yields the dioxide on washing and ignition. If a solution of stannic oxide be precipitated with ammonia a gelatinous precipitate is also obtained, which can be completely washed only with difficulty. If, however, it be heated with a concentrated solution of Glauber salt, a dense precipitate is thrown down, and this can be easily washed and yields the pure dioxide on ignition. An amorphous white or straw-yellow coloured powder is then obtained which is quite insoluble in water and possesses a specific gravity of 6·71. On heating it changes colour, becoming lemon-yellow and then brown, but it assumes its original tint on cooling.

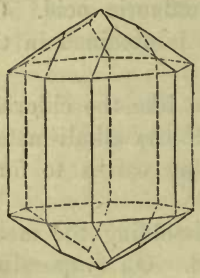

FIG. 163.

By heating amorphous stannic oxide in a current of hydrochloric acid gas it may be obtained in microscopic crystals which have the form of cassiterite and a specific gravity of 6·72 (Deville).[1] The formation of crystallized stannic oxide has been observed in fusing the dross collected on the hearth of a gun-metal furnace. The crystals were hard, brittle, four-sided prisms.[2] Stannic oxide can only be fused at a very high temperature. It is not volatile, nor is it attacked by concentrated acids, with the exception of sulphuric acid, with which it forms a syrupy liquid, the dioxide being again deposited on dilution with water.

Stannic Hydroxides. Two of these compounds are known, and these are distinguished, not by a difference in the proportion between anhydrous oxide and water, but by a variation in their physical properties. They both form salts with the alkalis, distinguished as *stannates* and *metastannates.*

488 *Stannic Acid and the Stannates.* Stannic acid is obtained as a white hydrated precipitate when calcium carbonate, not in excess, is added to a solution of stannic chloride, or when a stannate is carefully precipitated with an acid. The well-washed compound is slightly soluble in water and reddens blue litmus. Dried over sulphuric acid or in a vacuum, a compound is obtained which has the composition H_2SnO_3. This, on heating, gradually loses water, stannic oxide remaining behind. If

[1] *Comptes Rendus*, liii. 161. [2] Abel, *Chem. Soc. Journ.* x. 119.

ammonia be added to tin tetrachloride, $SnCl_4$, a gelatinous precipitate is obtained, which, when allowed to dry spontaneously, forms a glassy mass of stannic acid. Stannic acid dissolves readily in hydrochloric, nitric, and sulphuric acids, as well as in alkalis.

Soluble Stannic Acid was obtained by Graham[1] by the dialysis of a mixture of tin tetrachloride and alkali or of sodium stannate and hydrochloric acid, the gelatinous mass which is first formed gradually dissolving. The liquid is converted on heating into soluble metastannic acid. Traces of hydrochloric acid or of a salt bring about gelatinization in both solutions.

The stannates of the alkali-metals are the only ones which are soluble in water. The other stannates are obtained as insoluble precipitates by double decomposition.

Potassium Stannate, K_2SnO_3, is obtained by fusing the dioxid with potash or by dissolving the hydrated oxide in potash-ley. The solution yields on evaporation over sulphuric acid colourless glistening monoclinic prisms of $K_2SnO_3 + 3H_2O$ (Marignac), which have an alkaline taste and are readily soluble in water. Metallic copper brought into contact with the solution becomes covered with a bright coating of metal.

Sodium Stannate, Na_2SnO_3, is prepared on a large scale and employed extensively in calico-printing under the name of *preparing salts*. It is obtained either by fusing the finely-powdered or levigated tin-stone with caustic soda, dissolving the mass in water to remove any ore that may be unacted upon, and evaporating the solution; or by heating tin with caustic soda and Chili saltpetre. On evaporating the solution hexagonal crystals of $Na_2SnO_3 + 3H_2O$ are obtained, which are more soluble in cold than in hot water. A tolerably concentrated solution of the salt which contains no caustic soda deposits on cooling fine prisms of the composition $NaS_2nO_3 + 10H_2O$, and these effloresce on exposure to air.

489 *Metastannic Acid and the Metastannates.* In his *Reflections on the Hypothesis of Alkali and Acidum*,[2] published in 1670, Boyle remarks that aqua-fortis eats up or destroys more tin than it dissolves. On the other hand, he elsewhere[3] mentions that a solution of tin in aqua-fortis readily becomes gelatinous. Kunkel, who also studied the action of nitric acid on tin, mentions in his *Laboratorium Chymicum* that

[1] *Phil. Trans.* 1861, 213. [2] Boyle, *Op.* iv. 284.
[3] "Experiments and Considerations Concerning Colours."

tin can only be dissolved when it is added in small quantities to an acid, and that heat must be altogether avoided, because white calx of tin is thrown down when the acid is hot. The explanation of these different statements is to be found in the facts that when the metal is treated with weak nitric acid it forms either stannous or stannic nitrate according to the degree of concentration of the acid; and that the latter salt easily decomposes with separation of a gelatinous stannic acid, whilst, on the other hand, when tin is acted upon by strong nitric acid it is violently attacked with evolution of heat and formation of an insoluble white powder consisting of metastannic acid.

Metastannic acid reddens litmus, and when dried in the air contains about 20 per cent. of water, which it gradually loses when heated or when dried in a vacuum, during which process, however, no definite hydrate appears to be formed. According to R. Weber,[1] however, this compound when dried over sulphuric acid possesses the formula H_2SnO_3. But as the salts of metastannic acid all exhibit a complicated composition the formula of the acid is frequently represented by the formula $H_{10}S_5O_{15} = 5H_2SnO_3$. Weber, on the other hand, considers both stannic and metastannic acid to possess the same composition. Metastannic acid is distinguished from ordinary stannic acid, inasmuch as it is altogether insoluble in nitric acid, and swells up but does not dissolve in strong sulphuric acid, forming a compound with it which is decomposed by water. When warmed with concentrated hydrochloric acid it combines with it to form hydrochlorate of metastannic acid, which is insoluble in hydrochloric acid but solublein water, and which on boiling gelatinizes even in very dilute solution.

The salts of metastannic acid are formed by the action of the alkalis on metastannic acid or on its compound with hydrochloric acid. They all possess a very complicated composition and crystallize with difficulty. The sodium salt has been most exactly examined.

Sodium Metastannate, $Na_2Sn_5O_{11} + 4H_2O$, or $H_8Na_2Sn_5O_{15}$. This is a slightly soluble granular crystalline powder obtained by the action of cold caustic soda-ley on metastannic acid. If a hydrochloric acid solution of metastannic acid be precipitated with caustic soda hard gum-like masses of a compound $Na_2Sn_9O_{19} + 8H_2O$ are obtained. The existence of this last salt, and of several others having a still more complicated

[1] *Pogg. Ann.* cxxii. 358.

composition, renders it improbable that the true composition of the free acid is represented by the formula $H_{10}Sn_5O_{15}$. The metastannates in all probability possess a constitution similar to that of the more complicated silicates.

490 *Tin Tetrachloride* or *Stannic Chloride*, $SnCl_4$, was first mentioned by Libavius in 1605, who obtained it by distilling tin or its amalgam with corrosive sublimate. It was termed by him *Spiritus argenti vivi sublimati*, but afterwards it received the name *Spiritus fumans Libavii*. For its preparation the process originally proposed by Libavius may be employed, or chlorine may be passed over tinfoil or fused tin placed in a retort. When the stream of chlorine is quick, and especially if the gas-delivery tube dip into the molten metal, an evolution of light and heat is observed.

Tin tetrachloride is a colourless, thin, fuming liquid, which does not solidify at $-29°$, has a specific gravity of 2·234 at 15°, and boils at 120°, forming a colourless vapour having a specific gravity of 9·1997 (Dumas). At the boiling-point it dissolves rhombic sulphur, colourless phosphorus, and iodine, and can be mixed in all proportions with bromine and carbon disulphide. When mixed with turpentine so much heat is evolved that the hydrocarbon takes fire. Its property of fuming in the air depends on the fact that it absorbs atmospheric moisture. In 1770 Demachy observed that it solidifies when brought into contact with one-third of its weight of water to form a crystalline mass, termed *butter of tin*. Several distinct hydrates soluble in water may be produced, according to the quantity of water which is added. Thus the compound $SnCl_4 + 3H_2O$ is formed by exposing the anhydrous chloride to the action of moist air, or by the evaporation of its aqueous solution. This hydrate crystallizes in monoclinic needles which melt at 80°, and on cooling again solidify to a crystalline mass. A second hydrate, having the composition $SnCl_4 + 5H_2O$ is obtained by the addition of a sufficient quantity of water to the anhydrous chloride or by the gentle evaporation of the aqueous solution. It is deposited in opaque, acute, monoclinic prisms, which melt at a low temperature and again solidify to a crystalline mass. Lastly, large transparent monoclinic crystals of the hydrate $SnCl_4 + 8H_2O$ deposit in the cold from dilute solutions. On boiling a dilute aqueous solution of tin tetrachloride, stannic hydroxide is formed, and in very dilute solutions this precipitate forms spontaneously on standing.

Tin tetrachloride is employed by the dyer as a valuable mordant. Drebbel in Holland is said to have made the discovery that by help of this salt a permanent red dye can be obtained from cochineal. The dyers were formerly in the habit of preparing this mordant, known by the old names of tin-composition, physic, or dyer's spirits, by dissolving tin, together with sal-ammoniac or common salt, in nitric acid, or by dissolving tin in aqua regia, whence the solution was formerly termed nitro-muriate of tin. It is usual now for the dyers to employ the crystalline pentahydrate, $SnCl_4 + 5H_2O$, which is a commercial product known as *oxymuriate of tin.*

Anhydrous stannic chloride combines with ammonia to form a solid mass having the composition $SnCl_4(NH_3)_2$ (Rose), which can be sublimed and is soluble in water without decomposition. It can be obtained in crystals by evaporating the aqueous solution over sulphuric acid, but if it be allowed to stand for some days, or if the liquid be warmed, stannic hydroxide separates out in a gelatinous form. Tin tetrachloride also combines with many other chlorides to form crystalline compounds,[1] such as $SnCl_4 + 2SCl_4$. This is obtained by the action of chlorine on tin disulphide, and forms large yellow crystals, which melt at a summer temperature, liquefy at 30°, and decompose above 40°, with evolution of chlorine. If dry nitrous fumes be led into a solution of stannic chloride, the compound $SnCl_4 + N_2O_3$ is deposited as a yellow amorphous mass, and if this be sublimed, or if the dry vapours from aqua regia be passed into the chloride, the compound $SnCl_4 + 2NOCl$ is produced, which crystallizes in bright shining octohedrons. Stannic chloride also combines with phosphorus pentachloride to form the compound $SnCl_4 + PCl_5$, which sublimes in glistening colourless crystals, but when kept even in closed vessels it falls to an amorphous powder. It has a peculiar extremely pungent smell, and fumes strongly in the air. The compound $SnCl_4 + POCl_3$ forms crystals which melt at 58° and can be distilled at 180° without decomposition. This compound fumes strongly in the air, and is at once decomposed in contact with water.[2]

Ammonium Stannic Chloride, $2NH_4Cl + SnCl_4$, is deposited, when concentrated solutions of the two salts are mixed, in the form of a white powder, which can be recrystallized from dilute solution in small regular permanent octohedrons. It dissolves

[1] H. Rose, *Pogg. Ann.* xlii. 517.
[2] Casselmann, *Ann. Chem. Pharm.* lxxxiii. 257.

at the ordinary temperature in three parts of water. Its concentrated solution can be boiled without decomposition, but when diluted, tin hydroxide separates out. It was formerly much used by the calico-printer under the name of *pink-salt*, from its power of acting as a mordant for madder-red colours, but its use has been almost entirely superseded by the crystalline pentahydrated stannic chloride.

The other chlorides of the alkali-metals likewise form crystalline double salts with tin tetrachloride.

491 *Tin Tetrabromide*, or *Stannic Bromide*, $SnBr_4$. Tin and bromine unite together with evolution of light and heat. The action is moderated by adding the metal gradually to a solution of bromine in sulphide of carbon, or by adding bromine drop by drop to molten tin, when it burns with a pale violet flame. This compound is a white crystalline mass, which fumes strongly on exposure to air and is easily soluble in water. It melts at 30° and boils at 201°. The specific gravity of the liquid is 3·322 at 39° (Bödeker), and its vapour density is 7·92.[1] It is easily soluble in cold water, forming a colourless liquid from which the hydroxide is deposited slowly on standing at the ordinary temperature and quickly on boiling.

Tin Tetra-iodide, SnI_4. When tin and iodine are heated together a combination commences at 50°, and at a higher temperature heat and light are emitted. In order to prepare this compound tin filings are first moistened with carbon disulphide and then iodine gradually added. It crystallizes in red octohedrons, melting at 146° and having a specific gravity of 4·696. Tin tetra-iodide boils at about 300°, but sublimes at as low a temperature as 180° in yellowish-red needles, very similar in form to those of sal-ammoniac. It is soluble in carbon disulphide, absolute alcohol, ether, chloroform, and benzol, and is decomposed by water into hydriodic acid and stannic oxide.

492 *Tin Tetrafluoride* is not known in the free state. Hydrofluoric acid dissolves stannic hydroxide, the solution coagulating, like albumen, on boiling, and decomposing on evaporation with evolution of hydrofluoric acid. It forms crystalline double salts, termed stannofluorides, with many other fluorides, and these are isomorphous with the corresponding silicofluorides and titanofluorides.[2]

Potassium Stannofluoride, $K_2SnF_6 + H_2O$ is obtained by

[1] Carnelley and O'Shea, *Journ. Chem. Soc.* 1878, p. 55.
[2] Marignac, *Ann. Min.* [5], xv. 221.

neutralising hydrofluoric acid with potassium stannate. It crystallizes in thin mother-of-pearl glistening tablets, or in rhombic pyramids, which are much more soluble in hot than in cold water. When the solution contains an excess of hydrofluoric acid, the salt $K_2SnF_6 + HKF_2$ is deposited in thin monoclinic prisms.

Sodium Stannofluoride, Na_2SnF_6, forms glistening crystalline crusts.

Ammonium Stannofluoride, $(NH_4)_2SnF_6$, crystallizes in rhombohedrons, which are seldom perfect. Fine rhombic prisms of the compound $(NH_4)_2SnF_6 + 2NH_4F$ are deposited from a solution containing an excess of ammonium fluoride.

The stannofluorides of calcium and magnesium are also crystalline soluble salts.

The other stannic salts are but imperfectly investigated. *Stannic sulphate* is obtained by dissolving the hydroxide in sulphuric acid or by heating tin together with sulphuric acid, when a white mass remains behind on evaporating the solution. *Stannic nitrate* is obtained by dissolving stannic acid in nitric acid, and if the latter be not too dilute the nitrate crystallizes in silky tablets. Its solution coagulates when heated to 50°. *Stannic phosphate* is obtained by the action of phosphoric acid on the hydroxide, and is insoluble in water and in nitric acid. This reaction is employed for the separation of phosphoric acid from other bodies. For this purpose a known quantity of tinfoil is added to the nitric acid solution of the body under investigation, when the whole of the phosphoric acid remains behind with the metastannic acid.

TIN AND SULPHUR.

493 *Tin Monosulphide*, or *Stannous Sulphide*, SnS, is obtained by heating together the metal and sulphur. Thin tinfoil takes fire spontaneously when brought into sulphur vapour. When thus obtained it is a lead-gray tough crystalline mass, which melts at a higher temperature than the metal. When a solution of tin dichloride is saturated with sulphuretted hydrogen, a brown hydrated precipitate is obtained, which on drying becomes black. This is scarcely soluble in ammonium sulphide, but dissolves on the addition of sulphur, and is also soluble in the polysulphides of the alkali-metals. When the dried precipitate

is added to fused stannous chloride and the melted mass treated on cooling with dilute hydrochloric acid, stannous sulphide is obtained in metallic glistening crystalline scales, having a specific gravity of 4·973. Amorphous tin sulphide dissolves readily in hot hydrochloric acid; the crystallized substance dissolves less readily.

Tin Disulphide, or *Stannic Sulphide*, SnS_2. This compound, crystallizing in six-sided tablets or in gold-coloured translucent scales having a specific gravity of 4·425, is used as a bronze-powder for the purpose of bronzing articles of gypsum, wood, &c., and is known in commerce as mosaic gold. The discovery of this compound is usually ascribed to Kunkel. He does indeed speak of a sublimation of sulphide of tin and sal-ammoniac, but expresses himself so vaguely that it is impossible to recognise this compound from his description. It was well known in the eighteenth century under the names of mosaic gold, *aurum mosaicum*, or *musirum*. It was then prepared as it is at the present day by subliming a mixture of tin amalgam, sulphur, and sal-ammoniac, and as it was supposed to contain mercury it was often employed as a mercurial medicine. Peter Woulfe in 1771 showed that it did not contain mercury, and described other methods for its production according to which it is still prepared. Thus, for instance, it is obtained in the form of a fine pigment by heating eighteen parts of tin amalgam containing six parts of mercury with six parts of sal-ammoniac and seven parts of sulphur, when sal-ammoniac, mercuric chloride, and stannous chloride sublime and stannic sulphide remains behind in the form of golden-yellow scales. It is likewise prepared by heating tin monosulphide with eight parts of corrosive sublimate, or subliming tin filings with sal-ammoniac and sulphur, and according to several other receipts given by Woulfe.[1] Pelletier believed mosaic gold to be a compound of sulphur with the highest oxidation product of tin, and Proust, who found that it could be obtained by heating stannous chloride or tin monoxide with sulphur, supposed it to be a compound of tin, sulphur, and a small quantity of oxygen. The exact composition was ascertained by J. Davy and Berzelius in the year 1812. The formation of mosaic gold from tin, sulphur, and sal-ammoniac, appears to take place according to the following equations (Gmelin):

(I.) $Sn + 4NH_4Cl = (NH_4Cl)_2SnCl_2 + H_2 + 2NH_3$

(II.) $2(NH_4Cl)_2SnCl_2 + S_2 = SnS_2 + 2NH_4Cl + (NH_4Cl)_2SnCl_4$.

[1] *Phil. Trans.* 1771, p. 114.

When heated, a portion sublimes without decomposition, but the greater part is resolved into sulphur and monosulphide. It is not attacked by hydrochloric or nitric acid, but readily dissolves in aqua regia; as well as in caustic soda, when potassium stannate and potassium thiostannate are formed. If sulphuretted hydrogen be led into a solution of the tetrachloride a yellow precipitate is obtained. This consists of a mixture of tin disulphide and tin dioxide, and is readily soluble in the sulphides of the alkali-metals, when the *thiostannates* are formed. Of these the sodium salt has been obtained in the crystalline condition.[1] It is prepared by the addition of tin to fused sodium pentasulphide, when a violent reaction takes place. The mass is then lixiviated, and on evaporating the aqueous solution at a moderate temperature the compound $Na_2SnS_3 + 2H_2O$ is deposited in yellow vitreous regular octohedrons. When sodium sulphide is fused together with tin monosulphide and sulphur, a black crystalline mass is obtained yielding a dark-coloured solution, which on concentration at a low temperature yields colourless crystals resembling gypsum, and having the formula $Na_4SnS_4 + 12H_2O$.

Thiostannic Acid. When dilute hydrochloric acid is added to a solution of a thiostannate, a yellow precipitate is obtained, which on drying forms an almost black powder possessing a brown streak and wax-like lustre, and having the composition H_2SnS_3. When heated in absence of air it yields the golden-yellow disulphide.

When mosaic gold is fused with iodine in absence of air, a crystalline mass of SnS_2I_4 is obtained, and this can be sublimed in a current of carbon dioxide in dark-yellow glistening crystals, and may be recrystallized from solution in carbon disulphide, when large crystals, having the colour of potassium dichromate, are obtained. It is decomposed slowly by cold, but more rapidly by hot water, into stannic oxide, sulphur, and hydriodic acid.

TIN AND PHOSPHORUS.

494 When finely divided tin is heated in the vapour of phosphorus, a silver-white very brittle mass, having the composition SnP_3 is obtained. This has a specific gravity of 6·56, dissolves easily in hydrochloric acid, but is not attacked by nitric acid. When phosphorus is thrown on to the surface of molten tin,

[1] Kühn, *Ann. Chem. Pharm.* lxxxiv. 110.

combination also takes place. The compound containing the largest quantity of phosphorus which can thus be obtained has a silver-white colour, is not very brittle, and may be cut with a knife; it appears to possess the composition Sn_3P_2 (Pelletier). If spongy tin, obtained by precipitating a tin salt with zinc, be brought into contact with such a quantity of phosphorus that one atom of the latter be present to nine atoms of the metal, a phosphide having the composition Sn_9P is obtained. The same compound is formed whenever any of the other phosphides containing more phosphorus are heated. This is a coarse crystalline mass, which has the appearance of cast-zinc. It melts at 370°, and is used for the preparation of phosphor-bronze.

Detection and Estimation of Tin.

495 When a small quantity of a tin compound is held in the reduction-flame on a carbonized match, a malleable bead of metal is obtained, which easily dissolves in hot hydrochloric acid. This solution gives with mercuric chloride first a white and afterwards a black precipitate:

$$\text{(I.)}\quad SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$
$$\text{(II.)}\quad SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2Hg.$$

If one of the metallic globules be fused in a borax bead slightly tinted with cupric oxide and heated in the reduction-flame, the bead will become of a red tint, due to the formation of cuprous oxide.

Stannous salts yield a brown precipitate of stannous sulphide with sulphuretted hydrogen, which does not dissolve in colourless, but is soluble in yellow sulphide of ammonium, and from this solution hydrochloric acid precipitates the yellow disulphide. Both ammonia and caustic soda give white precipitates with the stannous salts. In the latter case the precipitate is soluble in an excess of the reagent.

Stannic salts are precipitated yellow by sulphuretted hydrogen. Stannic sulphide is readily soluble in ammonium sulphide. Alkalis precipitate a white hydroxide which dissolves in an excess of the precipitant.

Zinc precipitates metallic tin from solutions of the tin salts in the form of glistening scales or in a spongy or arborescent mass. The tin salts do not impart to the non-luminous gas-flame any colour, but the spark-spectrum of the chloride exhibits

two characteristic lines, having wave-lengths of 4526 and 5631 (Lecoq de Boisbaudran). These same lines are seen together with others in the spark-spectrum of the metal, the most brilliant of the tin lines being as follows (Thalén):

6452	5631	5563
5798	5588	4526

In the processes of qualitative analysis tin is obtained together with those metals which are precipitated by sulphuretted hydrogen in an acid solution. To separate tin from these the well-washed precipitate is treated with yellow sulphide of ammonium, filtered, and the filtrate acidified with cold dilute hydrochloric acid. The precipitate may contain, besides tin sulphide, the sulphides of arsenic and antimony. After it has been well washed with water, it is digested with solid carbonate of ammonium to dissolve the sulphide of arsenic. The residue is then heated with hydrochloric acid, and a slip of platinum-foil, upon which a small piece of zinc rests, is brought into the solution. The tin is thus deposited upon the zinc in a spongy mass. This is then dissolved in hydrochloric acid, and the usual tests applied.

Tin is determined *quantitatively* as the oxide. If the metal or one of its alloys be under examination, it is oxidized with pure, tolerably strong nitric acid, and the well-washed residue ignited. From solution it is precipitated with ammonia as the hydroxide, but if it be present in the form of stannous salt it must be first oxidized with chlorine or hydrochloric acid and potassium chlorate. The precipitate obtained by ammonia is then dissolved in the smallest quantity of hydrochloric acid, and heated with a concentrated solution of Glauber salt, when the hydroxide is again precipitated, and this is not gelatinous, and may therefore be easily washed (Löwenthal).

When tin sulphide is obtained in the separation of tin from the other metals, it can be gradually converted by gentle roasting and subsequent ignition into stannic oxide.

The *atomic weight* of tin was determined by Dumas by oxidizing the metal with nitric acid, his experiments giving the number 117·71,[1] whilst by the analysis of the tetrachloride he obtained the number 117·77.[2] Vlaanderen[3] obtained the number 117·86 by the reduction of the oxide by means of hydrogen.

[1] *Compt. Rend.* xlv. 409. [2] *Ann. Chim. Phys.* [3], lv. 129.
[3] *Scheid. Verhand. u. Onderzockingen Decl.* ii. *Stuk*, 150.

TITANIUM, Ti = 48.

496 The Rev. William Gregor[1] in 1789 discovered a new metal contained in the mineral menachanite or ilmenite, occurring in Cornwall. In 1795 Klaproth investigated the composition of the mineral rutile, and discovered in it a new metal to which he gave the name of titanium. In a subsequent investigation of ilmenite in 1797, he found that the metal which that mineral contained was titanium. Klaproth found that rutile consists mainly of titanium dioxide, but he did not succeed in obtaining the oxide in the pure state, this having been first accomplished in 1821 by Rose.

Titanium is a rare metal, and is not found in the metallic state. It occurs as the dioxide TiO_2 in three minerals, rutile, brookite, and anatase, which possess different crystalline forms (see Vol. I., p. 745), and also in combination with ferrous and ferric oxides in titanic iron or ilmenite $(FeTi)_2O_3$; and with lime and oxide of iron in perofskite $(CaFe)TiO_3$, as well as in titanite or sphene, $CaTiSiO_5$; schorlomite, $Ca(TiFe)SiO_5$, and keilhauite, $CaY(TiAlFe)SiO_5$. Magnetic iron also frequently contains larger or smaller quantities of titanium dioxide, and this titanium finds its way into many blast-furnace slags and pig-irons. Titanium occurs in small quantity in several other minerals, and traces have been found in trap and basalt, in many amphiboles and micas, in garnet, and hence it occurs in most fertile soils, in many clays, and likewise in certain mineral waters. It does not appear to form part of the animal or vegetable kingdom, but its presence has been detected in certain meteorites, and it forms an important constituent of the solar atmosphere.

497 *Metallic Titanium* is distinguished from almost all other elements by its singular power of combining at a high temperature with nitrogen. Hence the metal cannot be prepared in the pure state by any of the ordinary methods in the carrying out of which the atmospheric nitrogen is present, and consequently the first attempts to produce the metal yielded titanium nitride. Berzelius'[2] method of preparing metallic titanium consists in heating a mixture of dry potassium titanofluoride and potassium in a covered crucible, when titanium is reduced with incandescence. The fluoride of potassium is then removed by water,

[1] *Crell. Ann.* 1791. [2] *Pogg. Ann.* iv. 3.

and the metal obtained in the form of a dark-gray amorphous powder. Prepared in this way, however, titanium almost always contains titanium nitride. In order to obtain the pure metal, a tube of porcelain or hard glass is filled with hydrogen, and into this two boats are brought, one containing the double fluoride of potassium and titanium, and the other dry sodium. When all the air has been expelled by a current of hydrogen, the tube is heated so that the vapour of sodium comes in contact with the titanium salt, when the metal is reduced. The mass when cold is treated with warm water.[1] When dry potassium titanofluoride is heated with sodium in a well-closed porcelain crucible, titanium is obtained as a black porous mass, showing in different places brass-yellow or bronze-coloured particles.[2]

Titanium is a dark-gray amorphous powder closely resembling reduced iron in appearance. It possesses a bright metallic lustre and an iron-gray colour. When heated in the air it burns brightly with formation of titanium dioxide, and also of some nitride, and when thrown into flame in the state of fine powder it burns as brightly as uranium. When heated in oxygen it ignites with a blinding flash, forming a powder of titanium dioxide. Chlorine does not act upon titanium at the ordinary temperature, but at higher temperatures these elements combine with evolution of heat (Wöhler). Mixed with red lead and heated, it burns with such violence that the mass is thrown out of the crucible with loud detonation. Titanium does not decompose water at ordinary temperatures, but on heating the water to the boiling-point hydrogen begins to escape. It is readily soluble in warm hydrochloric acid with evolution of hydrogen, whilst dilute nitric, sulphuric, and even acetic acids attack the metal. When titanium is oxidized by nitric acid having a specific gravity of 1·25, much of the titanic acid formed remains insoluble.

TITANIUM AND OXYGEN.

498 Titanium forms several oxides, of which the most important is:—

Titanium Dioxide, TiO_2, which occurs as three different minerals, namely, rutile, brookite, and anatase, which all

[1] Wöhler and Deville, *Gött. Nachr.* 1857, p. 237.
[2] Glatzel, *Ber. Deutsch. Chem. Ges.* ix. 1829.

crystallize in the quadratic system. Rutile crystallizes in quadratic prisms (Fig. 164) and is isomorphous with cassiterite. These have an adamantine lustre, a brown or reddish colour, and a specific gravity of 4·18 to 4·25. They occur in granite, syenite, and gneiss, and occasionally in granular limestone and dolomite. Anatase has the same composition as rutile, but crystallizes in a totally different form (Fig. 165). It possesses a specific gravity of 3·82 to 3·95 and has a brown or black colour. The specific gravity of brookite is 3·86 to 4·23. These as well as the amorphous titanium dioxide can be artificially prepared. Amorphous titanium dioxide is obtained by the decomposition of aqueous chloride of titanium by ammonia, the precipitate being washed, dried, and ignited; or it may be directly prepared from rutile or titanic iron-ore. In order to prepare the pure oxide from rutile, the finely-powdered mineral is fused with three times its weight of carbonate of potash, the solidified mass powdered and dissolved, in a platinum vessel, in dilute hydrofluoric acid, in which case potassium titanofluoride is formed, and the iron separated out free from titanium. The mass is then heated with the addition of enough water to dissolve the whole of the titanium double salt, the liquid boiled and filtered hot. On cooling, the mass of the titanofluoride crystallizes out, and this, after washing with cold water, may be purified by re-crystallization. The titanofluoride is then dissolved in hot water, and the titanium precipitated by ammonia as titanic hydrate containing ammonia, and this on ignition yields pure titanium dioxide (Wöhler). Pure titanic oxide may also be obtained from titanic iron ore by igniting it in a mixture of chlorine and hydrochloric acid when ferric chloride is volatilized (Friedel and Guérin):

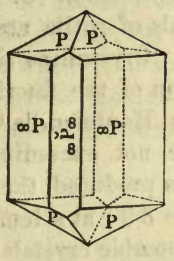

Fig. 164.

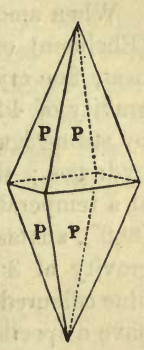

Fig. 165.

$$2FeTiO_3 + 4HCl + Cl_2 = Fe_2Cl_6 + 2TiO_2 + 2H_2O.$$

Titanium dioxide is a white tasteless powder, which when gently heated has a lemon-yellow colour, and when strongly ignited appears brown. It has a specific gravity of from 3·89 to 3·95,

and when very strongly heated its specific gravity rises to 4·25. It may be fused in the oxyhydrogen flame. It is not soluble in water, hydrochloric acid, or dilute sulphuric acid, even when heated for some time in them, but dissolves when digested for some time with strong sulphuric acid. It also dissolves slowly when fused with hydrogen potassium sulphate, a clear mass being obtained which dissolves perfectly in warm water. When fused with alkaline carbonates it yields the titanates.

When amorphous titanic oxide is heated with microcosmic salt (Ebelmen) or with borax (G. Rose) for some time to a white-heat, fine crystals of rutile are obtained, which have a specific gravity of 4·26. Crystalline titanic oxide can also be obtained by strong ignition of the fluoride in a current of moist air and hydrogen; thus Hautefeuille[1] has shown that by treatment at a temperature not exceeding the boiling-point of cadmium (860°), anatase is produced, the crystals of which have a specific gravity of 3·7 to 3·9; at a temperature of about 1,000°, steel-blue coloured, rhombic crystals of brookite are obtained, which have a specific gravity of 4·1, and closely resemble the natural crystals from Miask. At still higher temperatures again, rutile is produced, so that the latter is the only form which is stable at a high temperature, and in an acid or moist atmosphere.[2]

499 *Titanium Sesquioxide*, Ti_2O_3, is obtained by strongly igniting titanium dioxide in a current of hydrogen, and allowing the product to cool in the gas. The same oxide may also be obtained as a copper-coloured lustrous crystalline mass, together with the sesquichloride and oxychloride of titanium by passing a mixture of hydrogen and the vapour of titanium chloride over white-hot titanium dioxide. It is not attacked by nitric or hydrochloric acid, and sulphuric acid dissolves it with formation of a violet solution (Ebelmen).

The *hydrated sesquioxide* is formed by digesting a solution of titanic acid in hydrochloric acid with metallic copper at from 20° to 40°, when the solution attains a violet-blue colour, and this is then poured into aqueous ammonia, when a dark-brown precipitate of titanous hydroxide falls down (Fuchs). The hydroxide is also formed when a solution of the trichloride is precipitated by alkalis. The only known compound corresponding to the sesquioxide is the sesquichloride Ti_2Cl_6 (see page 260).

[1] *Ann. Chim. Phys.* [4], iv. 129.
[2] Friedel and Guérin, *Bull. Soc. Chim.* [2], xxii. 482.

Ilmenite, or *Titanic Iron-ore*, $(FeTi)_2O_3$. This mineral, the one in which titanium was first discovered, occurs tolerably widely distributed, and crystallizes in black hexagonal crystals, isomorphous with hæmatite. One of its most important localities is Krageroe, in Norway. Fine crystals are also found at Warwick Co., New York, and vast deposits occur at Bay St. Paul, in Canada. It is frequently found in the finely-divided state as sand on the shores of the Mersey opposite Liverpool, in New Zealand, and elsewhere. Its specific gravity ranges from 4·5 to 5, and its composition is a variable one. It is usually considered to be a mixture of ferrous titanate with ferric oxide, but its isomorphism with the latter, and the fact that when it dissolves in acids it yields the same colour as titanium sesquioxide renders Rose's view probable that it is an isomorphous mixture of the sesquioxides of iron and titanium.

TITANIC ACID AND THE TITANATES.

500 Titanium dioxide forms two acids or hydroxides which are termed titanic and metatitanic acids. These, however, have not been obtained of definite composition, nor have two corresponding series of salts been prepared.

Titanic Acid. This is obtained as a white powder, easily soluble in sulphuric, nitric, and hydrochloric acids, even when these acids are diluted, by precipitating a cold solution of titanium dioxide in hydrochloric acid with an alkaline hydroxide.

Metatitanic Acid. This is precipitated when acid solutions of titanium dioxide are boiled; it may also be prepared by acting on metallic titanium with nitric acid of specific gravity of 1·25. Titanic acid is also converted into metatitanic acid when dried in a vacuum, or heated in the air to 140°. It is a soft white powder, insoluble in water and almost insoluble in acids, with the exception of concentrated sulphuric acid.

Titanic hydroxide acts as a weak base as well as an acid, forming salts with both acids and alkalis.

Potassium Titanate, K_2TiO_3, is formed as a yellow fibrous mass when the dioxide is fused with potassium carbonate. On boiling titanic acid with caustic potash, colourless, readily soluble prisms of $K_2TiO_3 + 4H_2O$ are deposited. When a hydrochloric acid solution of titanic acid is precipitated with potassium carbonate, an amorphous precipitate of potassium trititanate

$K_2Ti_3O_7 + 2H_2O$, is thrown down, and this in presence of hydrochloric acid is converted into a hextitanate, $K_2Ti_6O_{13} + 2H_2O$. The fused anhydrous normal salt, when treated with water in excess, also yields a trititanate, $K_2Ti_3O_7 + 3H_2O$, as a fine crystalline powder.

Calcium Titanate, $CaTiO_3$. This occurs in the Urals, in the valley of Zermatt in Switzerland, and at Magnet Cove, Arkansas, as the mineral perofskite, which contains in addition 1 to 6 per cent. of ferrous oxide, as well as traces of manganese and magnesium. It forms rhombic crystals having a metallic or adamantine lustre, a yellow or iron-black colour, and a specific gravity of 4·0. The crystals can be artificially obtained by strongly igniting a mixture of titanium dioxide, lime, and calcium carbonate (Ebelmen).

Calcium Titanosilicate, $CaTiSiO_5$, is found as titanite or sphene in brown, green, or black monoclinic crystals, having an adamantine or resinous lustre and a specific gravity of 3·4 to 3·56, occurring imbedded in granite, gneiss, mica-schist, and granular limestone. Titanite can be obtained artificially by fusing calcium chloride with titanium dioxide and silica. The mineral guarinite has the same composition as titanite, and is found in quadratic crystals, having a specific gravity of 3·487, in small cavities in a grayish trachyte at Monte Somma.

THE SALTS OF TITANIUM.

501 *Titanium Dichloride*, $TiCl_2$, was obtained by Friedel and Guérin[1] by passing dry hydrogen at a dark-red heat over titanium sesquichloride. This compound is a very hygroscopic light-brown powder, which can be volatilized in hydrogen at a red-heat without fusion. It burns like tinder on exposure to air, giving off fumes of titanium tetrachloride and leaving a residue of titanium dioxide. It hisses when thrown into water, evolving hydrogen and yielding a yellow liquid.

Titanium Sesquichloride, Ti_2Cl_6. When the vapour of titanium tetrachloride mixed with hydrogen is passed through a red-hot tube, dark violet scales of the sesquichloride are deposited (Ebelmen). It may also be obtained by heating titanium tetrachloride

[1] *Ann. Chim Phys.* [5], vii. 24.

in a closed tube with molecular silver to a temperature of from 180° to 200°:

$$2TiCl_4 + 2Ag = Ti_2Cl_6 + 2AgCl.$$

If the mixture thus obtained be heated more strongly, the reverse action takes place (Friedel and Guérin). Titanium sesquichloride is non-volatile and on heating decomposes into the dichloride and tetrachloride. When heated in the air, thick vapours of titanium tetrachloride are emitted and titanium dioxide is left behind. It readily deliquesces on exposure to moist air, and dissolves in water with evolution of heat, yielding a reddish-violet solution.

Titanium sesquichloride is a powerful reducing agent. Thus when boiled with aqueous sulphurous acid, sulphur separates out, and the salts of gold, silver, and mercury are reduced by it to metal.

502 *Titanium Tetrachloride*, $TiCl_4$. Metallic titanium does not combine with chlorine at the ordinary temperature, but when heated it burns in the gas with brilliancy, forming the tetrachloride (Wöhler). According to Friedel and Guérin, titanium dioxide is converted, in presence of chlorine at a white-heat, into titanium tetrachloride with evolution of oxygen. The tetrachloride is, however, best obtained by passing dry chlorine over a heated mixture of titanium dioxide and carbon. Titanium tetrachloride is a mobile, transparent, colourless liquid, having a specific gravity of 1·7609 at 0° (Pierre). It boils at 135°, and its vapour has a specific gravity of 6·836 (Dumas). It possesses a penetrating acid smell, and emits dense white fumes on exposure to air. The pure chloride remains liquid at −25°.

Titanium tetrachloride dissolves in water with evolution of heat, and when exposed to the air it absorbs moisture and gradually solidifies, forming hydrated titanium tetrachloride, which dissolves in a larger quantity of water. Titanium tetrachloride is not decomposed by potassium even at the boiling-point, but when its vapour is passed over heated potassium or sodium, metallic titanium is formed with incandescence.

Titanium tetrachloride yields a large number of crystalline compounds with other chlorides analogous to those formed by stannic chloride. When dry ammonia gas is passed over titanium tetrachloride, it is rapidly absorbed, and a very hygroscopic powder, $TiCl_4 + 4NH_3$, is formed, which when ignited yields a yellow sublimate of $TiCl_4 + 3NH_4Cl$.

Titanium Oxychloride, $Ti_2O_2Cl_2$, is obtained, together with dichloride, when a mixture of hydrogen and the vapour of titanium tetrachloride is passed over the ignited dioxide. It forms reddish-brown translucent crystals, which burn when heated in the air, with formation of dioxide and tetrachloride (Friedel and Guérin).

Titanium Tetrabromide, $TiBr_4$, is obtained when bromine is passed over a mixture of titanium dioxide and carbon at a red-heat. The brown crystalline product is rectified over mercury, and an amber-yellow, hygroscopic, finely crystalline mass is obtained which has a specific gravity of 2·6, melts at 39°, and boils at 230°.[1]

Titanium Tetraiodide, TiI_4, is produced when iodine vapour is passed over ignited titanium (Weber); also when dry hydriodic acid is passed into titanium tetrachloride, which is gradually heated up to its boiling-point. The small quantity of free iodine giving a violet tinge may be removed by three or four distillations in a stream of hydrogen (Hautefeuille). A third process consists in passing the vapour of titanium tetrachloride mixed with hydrogen and iodine vapour through a tube heated to redness. Titanium tetraiodide forms a brittle mass having a reddish-brown colour and metallic lustre. It melts at 150° to a yellowish-brown liquid, which solidifies on cooling to fine octohedral crystals. It distils without decomposition at a temperature slightly above 360°, giving rise to orange-coloured vapours. The specific gravity of its vapour at 440° is 18·054. It fumes strongly in the air and dissolves readily in water.

503 *Titanium Tetrafluoride*, TiF_4, is obtained as a fuming, colourless liquid when a mixture of titanium dioxide and fluor-spar is distilled with fuming sulphuric acid in a platinum vessel (Unverdorben). When titanium dioxide is dissolved in hydrofluoric acid, a syrupy liquid is obtained, which is probably *hydrogen titanofluoride*, H_2TiF_6. The *titanofluorides* are isomorphous with the silicofluorides and zirconofluorides.

Potassium Titanofluoride, $K_2TiF_6 + H_2O$. This salt is prepared either by adding potash to aqueous hydrogen titanofluoride (Berzelius), or, according to Wöhler, by fusing titanium dioxide in a platinum crucible with twice its weight of potassium carbonate and dissolving the fused and pulverised mass, in a platinum dish, in the requisite quantity of dilute hydrofluoric acid. The potassium salt then crystallizes out in shining scales,

[1] Duppa, *Proc. Roy. Soc.* viii. 42.

closely resembling those of boric acid and belonging to the monoclinic system (Marignac), which may be dried between filter paper, and recrystallized from boiling water. It loses its water at 100°, and melts without decomposition at a white-heat.

Sodium Titanofluoride, Na_2TiF_6, is obtained in a similar manner to the preceding salt in hexagonal prisms most probably isomorphous with sodium silicofluoride (Marignac). A solution containing an excess of hydrofluoric acid deposits small glistening rhombic crystals having the composition $Na_2TiF_6 + NaHF_2$.

Ammonium Titanofluoride, $(NH_4)_2TiF_6$. This salt was obtained by Berzelius in rhombohedrons isomorphous with the corresponding tin compound, by neutralizing hydrogen titanofluoride with ammonia. A second ammonium salt having the composition $(NH_4)_2TiF_6 + NH_4F$ separates in quadratic crystals from a solution of the preceding salt in an excess of fluoride of ammonium.

The titanofluoride of strontium, $SrTiF_6 + 2H_2O$, is a soluble salt isomorphous with the corresponding silicofluoride, whilst magnesium titanofluoride, $MgTiF_6 + 6H_2O$, is isomorphous with the corresponding stannofluoride.

504 *Titanium Sesquisulphate*, $Ti_2(SO_4)_3 + 8H_2O$, is obtained by dissolving the metal in dilute sulphuric acid. The violet solution, which on concentration assumes a fine blue lustre, deposits small tufts of crystals (Glatzel).

Normal Titanium Disulphate, $Ti(SO_4)_2 + 3H_2O$, is formed by the oxidation of the sesquisulphate with nitric acid, and on evaporation remains as a transparent yellowish deliquescent amorphous mass. If the calculated quantity of potassium sulphate be added to this solution and the mixture allowed to evaporate over sulphuric acid, crystals of the double salt $K_2SO_4 + Ti(SO_4)_2 + 3H_2O$ separate out.

Basic Titanium Sulphate, $(TiO)SO_4$, is obtained as a white hard mass by dissolving dry titanic acid in boiling sulphuric acid and evaporating.[1]

Basic Titanium Phosphate, $Ti(OH)PO_4 + H_2O$, is obtained as a gelatinous precipitate by adding ammonium phosphate to a hydrochloric acid solution of titanic acid. On drying at 100° it attains the above composition. The *pyrophosphate*, $(TiO)_2P_2O_7$, is formed as a plant-like growth by igniting the preceding compound.

The soluble titanium salts possess a sour, very astringent taste.

[1] Merz, *Journ. Pract. Chem.* xcix. 157.

TITANIUM AND SULPHUR.

Titanium Sulphide, TiS_2. This compound, discovered by Rose, is the only known sulphide of titanium, and is prepared by slowly passing the vapour of carbon disulphide over titanium dioxide. It forms large brass-yellow lustrous scales, closely resembling mosaic gold. It burns when ignited in the air, yielding titanium dioxide and sulphur dioxide.

TITANIUM AND NITROGEN.

505 Titanium possesses the remarkable property of combining directly at high temperatures with free nitrogen (Wöhler). Several compounds of titaninm and nitrogen are known. The compound Ti_3N_4 is obtained by heating ammonio-chloride of titanium, $TiCl_4,4NH_3$. by itself (H. Rose), or better in a stream of ammonia gas[1] as a copper-coloured substance originally supposed to be metallic titanium, but which Wöhler[2] proved to consist of a nitride of titanium having the above composition and containing 8 per cent. of nitrogen.

Another nitride of titanium, TiN_2, is obtained as a dark-blue powder, having a copper-red lustre resembling sublimed indigo, by strongly igniting titanium dioxide in a current of ammonia gas (Wöhler).

A third compound, Ti_5N_6, is prepared by igniting the compound Ti_3N_4 in a current of hydrogen, when ammonia is given off. It possesses a bronze or almost golden-yellow colour, and may be heated to the melting-point of copper, air being excluded, without undergoing change, but when heated in nitrogen it combines again with it. Tissié du Mothay has proposed to utilise this reaction for obtaining ammonia from atmospheric nitrogen, inasmuch as these nitrides yield ammonia when heated in hydrogen.

When these nitrides in a finely-divided state are heated with the oxides of copper, lead, and mercury, they emit a sparkling flame, the oxides being reduced to the metallic state. When fused with caustic potash they are decomposed with evolution of ammonia (Wöhler).

[1] Liebig, *Pogg. Ann.* xxi. 259. [2] *Ann. Chem. Pharm.* lxxiii. 34.

According to the recent investigations of Friedel and Guérin, titanium only forms the compounds Ti_3N_2, Ti_3N_4, Ti_2N_2.

Titanium Cyano-nitride. When iron ores containing titanium are reduced in the blast-furnace, small brilliant copper-coloured cubes, which are hard enough to scratch glass, and are almost infusible, are found in cavities both of the slag and of the metal. A mass containing as much as 80 lbs. has been found in a single blast-furnace in the Harz. This substance was examined by Wollaston in 1822 and believed by him to be metallic titanium;[1] but Wöhler in 1849 showed that it contained nitrogen and cyanogen, and gave to it the formula $Ti(CN)_2 + 3Ti_3N_2$. He likewise obtained it artificially[2] by heating a mixture of ferrocyanide of potassium and titanium dioxide in a well-closed crucible at a temperature sufficient to melt nickel. Titanium cyano-nitride can also be prepared by heating to whiteness a mixture of titanium dioxide and charcoal in a tube of gas-carbon in a stream of dry nitrogen (Deville and Wöhler).[3] A third method of preparation is to fuse potassium cyanide in the vapour of titanium tetrachloride (Wöhler). The artificial crystals, which resemble the natural ones in crystalline form and colour, have a specific gravity of 5·28, and are only attacked by a mixture of nitric and hydrofluoric acids. When ignited in a current of steam they are decomposed as follows:

$$Ti(CN)_2 + 3Ti_3N_2 + 20H_2O = 2HCN + 10TiO_2 + 6NH_3 + 10H_2.$$

Chlorine also decomposes this substance at a red-heat, titanium tetrachloride and a volatile sublimate consisting of a compound of titanium tetrachloride and cyanogen chloride being formed. When fused with potash ammonia is given off, potassium titanate being produced.

Detection and Estimation of Titanium.

506 Titanium is distinguished from tin inasmuch as its oxides are not reduced to the metallic state when heated on charcoal before the blowpipe. With microcosmic salt titanium dioxide yields a colourless bead in the outer flame and in the inner flame the bead is yellow whilst hot but assumes a violet colour on cooling. According to Riley the delicacy of this reaction is increased by melting metallic zinc in the microcosmic bead heated on charcoal, a distinct colouration being then obtained,

[1] *Phil. Trans.* 1823, 17. [2] *Ann. Pharm.* lxxiii. 34, and lxxiv. 212.
[3] *Ann. Chem. Pharm.* ciii. 230.

when the zinc is burnt away, with minute quantities of titanium. When fused in the microcosmic bead with addition of a small quantity of an iron salt in the reducing flame a bright-red bead is obtained.

Titanium compounds do not colour the gas-flame, but the spark-spectrum shows an enormous number of bright lines, chiefly in the blue and green, which have been carefully mapped by Thalén and others. Metallic zinc placed in a hydrochloric acid solution of titanic acid evolves hydrogen and the liquid assumes a violet-blue colour, a dark violet precipitate being formed if the solution be not too dilute, and this gradually turns white by oxidation. The violet-blue solution when diluted with water assumes a rose-colour, and this reaction serves for the detection of small quantities of titanium. Sodium thiosulphate when boiled with a nearly neutral solution of a titanate precipitates the whole of the titanic acid, and this reaction serves as a means of separating titanium from iron and the metals of the cerium group.

Titanium is always determined *quantitatively* in the form of titanium dioxide this being thrown down from its solutions in acids by ammonia. Titanium may also be determined volumetrically by reducing titanium dioxide to titanium sesquioxide by means of zinc in an acid solution and subsequent oxidation by a standard permanganate.

The atomic weight of titanium was first determined by Rose[1] in 1829 by decomposing titanium tetrachloride with water, weighing the titanic acid and estimating the amount of chlorine in the filtrate; 100 parts of titanium tetrachloride yielded 301·7 parts of silver chloride, whence the atomic weight of titanium is found to be 48·15. Pierre,[2] on the other hand, in 1847 obtained the number 50·23, whilst Demsly[3] obtained the number 56·3.

Of these Rose's number is probably the most reliable. Titanium stands in the same relation to silicon as vanadium stands to phosphorus, and chromium to sulphur. It has, however, been observed in similar cases that the difference between the atomic weights of analogous elements is nearly constant and it would, therefore, appear that the lower atomic weight is the more likely to be correct.

Si = 28	P = 30·96	S = 31·98
Ti = 48	V = 51·2	Cr = 52·4

[1] *Pogg. Ann.* xv. 145. [2] *Ann. Chim. Phys.* [3], xx. 257.
[3] *Compt. Rend.* 1849, 325.

Titanium occupies a peculiar position amongst the metals. In consequence of its liquid volatile tetrachloride and of its acid-forming dioxide it stands in a mean position between silicon and tin, whilst, on the other hand, in its power of forming sesqui-compounds it is allied to iron, chromium, and aluminium.

ZIRCONIUM $Zr = 90$.

507 In 1789 Klaproth found a new earth in the mineral zircon, to which he gave the name of zirconium. He discovered in 1795 that the same earth was contained in hyacinth, a mineral found in Ceylon, and he thus ascertained the truth of Werner's previous supposition that these two minerals are identical. Zircon and hyacinth possess the formula $ZrSiO_4$, and are more or less coloured by ferric oxide. Zirconium is likewise found in a few other rare minerals.

The metal zirconium was first obtained by Berzelius in the form of an iron gray powder by heating potassium zirconofluoride with potassium. The metal also can be obtained, according to Troost, by passing the vapour of zirconium chloride, $ZrCl_4$, over ignited sodium. The ignited amorphous metallic powder thus obtained is so finely divided that it passes through the pores of filter-paper, but it assumes a metallic lustre under the burnisher. In the crystallized state zirconium was first prepared by Troost[1] by strongly heating potassium zirconofluoride with 1·5 times its weight of aluminium in a graphite crucible. The temperature employed must be high enough to fuse iron, otherwise the metal contains large quantities of aluminium. The excess of this latter metal is extracted with hydrochloric acid, and the brittle crystalline scales of zirconium remain undissolved. These resemble antimony in their appearance and have a specific gravity of 4·15. The following is the composition of the metal thus prepared:[2]

Zirconium	98·34
Aluminium	1·03
Silicon	0·17
	99·54

[1] *Bull. Soc. Chim.* i. 213. [2] Franz, *Ber. Deutsch. Chem. Ges.* iii 58.

The amorphous metal takes fire in the air when gently warmed and burns with a bright light, but the crystallized variety can only be ignited at the temperature of the oxy-hydrogen flame, or in chlorine gas at a red-heat. Ordinary acids do not attack it, even on heating, but it readily dissolves in hydrofluoric acid, and it is rapidly oxidized by aqua regia.

Zirconium Oxide or Zirconia, ZrO_2, is the only oxide of this metal. In order to prepare it, zircon is ignited and then quenched in water. The powdered mineral is mixed with three to four times its weight of acid potassium fluoride and gently heated in a platinum vessel until all moisture has been driven off. The platinum crucible is then placed in a Hessian one and both well covered and exposed for two hours to the strongest heat of a wind-furnace. The porcelain-like mass thus obtained is boiled with water containing hydrofluoric acid and the insoluble potassium silicofluoride filtered off. On cooling the solution, crystals of potassium zirconofluoride are deposited and these purified by recrystallization. The pure salt is then heated with sulphuric acid until all the hydrofluoric acid is driven off, dissolved in water, and the zirconia precipitated in the cold by ammonia.[1]

In order to avoid the use of hydrofluoric acid, the very finely powdered zircon may be treated as follows. It is first fused with hydrogen potassium sulphate and the fused mass repeatedly boiled out with water containing sulphuric acid when a residue of basic zirconium sulphate, Zr_3SO_9, is obtained, which is next fused with caustic soda in a silver basin. This is then lixiviated with water, the residual zirconia, which contains soda, washed with hot water and dissolved in hot concentrated sulphuric acid, the solution filtered and precipitated with ammonia (Franz). The precipitate thus obtained consists of *Zirconium Hydroxide*, $Zr(OH)_4$, which readily parts with its water on heating. The hydroxide is slightly soluble in water and colours yellow turmeric paper brown. When precipitated and washed in the cold it is easily soluble in acid. If, however, it be precipitated from a hot solution, or washed with boiling water, it is only soluble in concentrated acids. When heated to incipient redness it is converted into zirconia with evolution of heat. The oxide thus obtained is only slightly soluble even in hydrofluoric acid but dissolves on heating in a mixture of two parts of sulphuric acid and one part of water. Zirconia can be obtained in the

[1] Homberger, *Liebig's Ann.* clxxxi. 232.

crystalline state in the form of quadratic prisms isomorphous with cassiterite and rutile and having a specific gravity of 5·71.[1] For this purpose the amorphous oxide is fused with borax in a porcelain furnace, the fused residue being boiled out with sulphuric acid.

Like the oxides of the other metals of this group, zirconia forms salts with both acids and bases.

ZIRCONATES.

508 *Sodium Zirconate*, Na_2ZrO_3, obtained by fusing the oxide with carbonate of soda, forms a crystalline mass which is decomposed by water with separation of zirconia. When heated with an excess of sodium carbonate to whiteness the salt Na_4ZrO_4 is produced. This is again decomposed by water with formation of hexagonal tables having the composition $Na_2Zr_8O_{17} + 12H_2O = Na_2O.8ZrO_2 + 12H_2O$.

The zirconates of calcium and magnesium are crystalline and insoluble in water.

SALTS OF ZIRCONIUM.

509 *Zirconium Chloride*, $ZrCl_4$, is obtained as a white sublimate by igniting a mixture of zirconia and charcoal in a current of chlorine. The specific gravity of the vapour is 8.15.[2] It dissolves in water with evolution of heat, and on evaporating the solution the basic salt $2ZrOCl_2 + 9H_2O$ separates out in stellated needles. If the hydroxide be dissolved in hydrochloric acid, and the solution evaporated, silky needles are deposited which have an astringent taste. These lose water at 50° and are converted into the above basic salt. When the anhydrous chloride is heated in oxygen the oxychloride, $Zr_4O_2Cl_2$, is obtained in the form of a volatile white solid body.[3]

Zirconium Bromide, $ZrBr_4$, is prepared in a similar way to the chloride and forms a white crystalline powder which is easily volatilized at the heat of the gas-flame. In contact with moist air or water it forms zirconium oxybromide, $ZrOBr_2$, which crystallizes in needles.

[1] Nordenskiöld, *Pogg. Ann.* cxiv. 612.
[2] Deville and Troost, *Comptes Rendus.* xlv. 821.
[3] *Ibid.* lxxiii. 563.

Zirconium Fluoride, ZrF_4, is obtained by heating zirconia with acid ammonium fluoride. The residual mass is easily soluble in water containing hydrofluoric acid and crytallizes in glistening triclinic tables having the composition $ZrF_4 + 3H_2O$.

Zirconium fluoride forms a series of double salts with other fluorides which are isomorphous with the corresponding silicofluorides, stannofluorides, and titanofluorides.

Potassium Zirconofluoride, K_2ZrF_6, is obtained by igniting zircon with acid potassium fluoride or by pouring a solution of potassium fluoride into an excess of zirconium fluoride solution. It crystallizes from hot water in small acute rhombic prisms and dissolves at 2° in 128, at 15° in 71, and at 100° in 4 parts of water. This salt is used for the preparation of the metal.

When zirconium hydroxide is dissolved in the smallest quantity of hydrofluoric acid, and the liquid poured into a concentrated solution of neutral potassium fluoride, the salt $K_2ZrF_6 + KF$ is precipitated, and may be crystallized from boiling water in fine needles.

If sodium fluoride and zirconium fluoride be mixed in any proportion, the salt $Na_2ZrF_6 + 4NaF$ is produced. It forms small monoclinic crystals which dissolve in 258 parts of water at 18° and at 100° in about 60 parts of water.

Ammonium salts, corresponding to the salts of potassium, and other double fluorides, are known, which crystallize well and are usually soluble.

Zirconium Sulphate, $Zr(SO_4)_2$, is obtained by dissolving the oxide or hydroxide in sulphuric acid, evaporating, and heating nearly to redness. It is a white mass which dissolves slowly but completely in cold, and quickly in hot water. Hydrated crystals are obtained by concentrating a solution which contains free acid, and these swell up on heating like alum. The salt decomposes at a red-heat, leaving a residue of pure zirconia. If its solution be saturated with zirconium hydroxide a basic salt, $Zr(SO_4)_2 + ZrO_2$, is formed, and this is obtained on evaporation as a hydrated mass. If the normal salt be precipitated with alcohol an insoluble salt, $Zr(SO_4)_2 + 2ZrO_2$, is thrown down.

Zirconium Nitrate, $Zr(NO_3)_4$, is obtained as a yellow gummy mass by dissolving the hydroxide in nitric acid and evaporating at a moderate heat.

Silicates of Zirconium. Of these, zircon, $ZrSiO_4$, is the most important. It occurs in crystalline rocks, especially in granular limestone, schist, gneiss, syenite, and granite. The chief

localities are in alluvial sands in Ceylon, the Urals, in the Isle of Harris, in Greenland, in the gold districts of Australia, and in many places in North America. Zircon crystallizes in quadratic prisms and pyramids (Fig. 166) having an adamantine lustre and in the pure state are colourless. Usually, however, zircon is coloured red or yellow by ferric oxide. The colourless as well as the smoke-coloured variety is termed jargon. This variety exhibits a peculiar absorption spectrum, from which Sorby concluded that it contained a new element, to which he gave the name of jargonium, but subsequently he found that these lines are caused by the presence of uranium oxide. An artificial jargon yielded a similar spectrum, though neither uranium nor zirconium compounds do so.[1]

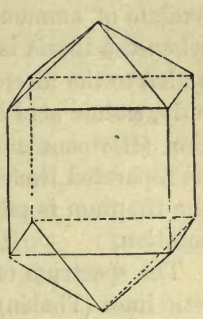

Fig. 166.

ZIRCONIUM AND SULPHUR.

When metallic zirconium and sulphur are heated together in a current of hydrogen, they combine with evolution of heat to form a cinnamon-brown powder, which assumes a metallic lustre under the burnisher. This is not attacked by most of the dilute acids, but dissolves slowly in aqua regia and readily in hydrofluoric acid. When fused with potash zirconia and potassium sulphide are formed.

Detection and Estimation of Zirconium.

510 The reactions of the zirconium salts are very similar to those of the metals contained in cerite and gadolinite. A reaction of zirconium by which it is distinguished from the cerium metals is the formation of a basic potassium-zirconium sulphate insoluble in water and hydrochloric acid. This salt is obtained by adding a hot solution of potassium sulphate to a concentrated solution of a zirconium salt. This reaction also serves to separate zirconium from titanium, tantalum, and niobium. Another method of separating zirconium from the metals of the cerium and iron groups is to boil the solution with sodium

[1] *Chem. News*, xxi. 73.

thiosulphate, when zirconium alone is precipitated as the thiosulphate; this on washing and heating leaves a residue of zirconia.

Titanic acid and thoria are also precipitated together with the zirconia by sodium thiosulphate. In order to separate these, oxalate of ammonia is added to the hydrochloric acid solution when the thoria is thrown down. Carbonate of ammonia is now added to the filtered liquid when, in the presence of the oxalate only, titanic acid is precipitated, the zirconia remaining in solution (Hermann). According to Franz and Streit, zirconia can be separated from titanic acid by boiling with acetic acid; all the titanium is precipitated, the zirconia and iron remaining in solution.

The spectrum of zirconium contains the following characteristic lines (Thalén):

6127 in the red.
4815, 4771, 4738, 4709, 4686 in the blue.

The *atomic weight* of zirconium has not yet been determined with accuracy. The analysis of the sulphate led Berzelius[1] to the number 89·2, whilst from analyses of the chloride Hermann[2] obtained the number 88·8. On the other hand, according to Marignac and Deville,[3] the above number is somewhat too low, the true atomic weight approaching more nearly to 90, which is therefore taken as the atomic weight of zirconium.

THORIUM = 231·5.

511 In the year 1815 Berzelius believed that he had found a new earth in several Swedish minerals, to which he gave the name of thoria, but on further examination the substance turned out to be basic phosphate of yttrium. On the other hand, in 1828,[4] he discovered a distinct earth in a mineral from the island of Lövön, in Norway, now termed thorite, and to this the name of thoria was given, as it agreed in many of its properties with the substance previously so named. Besides being found in thorite, this substance was discovered in other rare minerals; thus by Wöhler in pyrochlor, by Karsten in monazite, and by Bergmann and others in orangeite. Another source of thoria is the mineral

[1] *Pogg. Ann.* iv. 124, and viii. 186.
[2] *Journ. Pract. Chem.* xxxi. 77.
[3] *Ann. Chim Phys.* [3], lx. 263.
[4] *Pogg. Ann.* xvi. 385.

euxinite from Arendal, in which this earth was discovered by Mosander and Chydenius.

The following table gives the composition of some of these minerals:

Thorite from Lövön.		Orangeite from Langesundfiord.		Monazite from Ilmengebirge.	
SiO_2	19·31	SiO_2	17·76	P_2O_5	28·50
ThO_2	58·91	ThO_2	73·80	ThO_2	17·95
UO_3	1·64	PbO	1·18	SnO_2	2·10
Fe_2O_3	3·46	CaO	1·08	Ce_2O_3	26·00
Mn_2O_3	2·43	H_2O	6·45	La_2O_3	23·40
CuO	2·62		100·27	MnO	1·86
MgO	0·36			CaO	1·68
K_2O	0·15				101·49
Na_2O	0·11				
PbO	0·82				
SnO_2	0·01				
Al_2O_3	0·06				
H_2O	9·66				
	99·54				

Thorium also occurs in other minerals containing the metals of the cerium group, as gadolinite and orthite. In one of these minerals Bahr believed he had found another new metal to which he gave the name wasium, but he afterwards convinced himself that this substance is identical with thorium.[1]

Metallic Thorium is obtained by heating the chloride with potassium or sodium. Thus prepared it forms a grey powder which assumes an iron-grey lustre under the burnisher. It has a specific gravity of from 7·659 to 7.795, and takes fire when heated in the air, burning with a bright flame; it does not decompose even in boiling water, dissolves with difficulty in hydrochloric acid, and is not attacked by aqueous alkalis, but is readily soluble in nitric acid.

512 *Thorium Oxide or Thoria*, ThO_2, is obtained from thorite or orangeite by heating the finely-powdered mineral with hydrochloric acid, evaporating the solution to dryness, moistening the dry residue with hydrochloric acid and lixiviating with hot water. The solution is then treated with sulphuretted hydrogen, the liquid filtered from the precipitated sulphides, and the filtrate

[1] *Ann. Chem. Pharm.* cxxxii. 227

precipitated with ammonia. The precipitate is next dissolved in the smallest quantity of hydrochloric acid, and the solution mixed with a solution of potassium sulphate. The insoluble potassium thorium sulphate, which separates out, is dissolved in hot water, and the hydroxide precipitated as a gelatinous mass by ammonia. On drying at 100° this possesses the composition $Th(OH)_4$, and on ignition leaves a residue of the dioxide. The latter can be obtained in quadratic crystals isomorphous with cassiterite and rutile by heating the amorphous powder with borax in a porcelain furnace. These possess a specific gravity of 9·2, and only dissolve in concentrated sulphuric acid after long boiling.

Meta-thorium Oxide. This is obtained by igniting the oxalate, and its peculiar deportment with volatile acids explains the fact that Bahr believed this to be the oxide of a new metal. If it be treated with hydrochloric acid or nitric acid no apparent action takes place, but if an excess of acid be evaporated on the water-bath, a brownish semi-transparent residue is left, and this dissolves in water to form a translucent opalescent liquid which appears milk-white in reflected light, and from which a small quantity of nitric or hydrochloric acid precipitates the oxide. If the solution be precipitated with ammonia and the precipitate dried at 100°, a compound having the composition $Th_4O_7(OH)$ is obtained and this is insoluble in acids.[1]

THE SALTS OF THORIUM

513 Are colourless, and those which are soluble possess a strongly astringent taste.

Thorium Chloride, $ThCl_4$. This is obtained by heating the oxide mixed with carbon in a current of chlorine. It forms a slightly volatile mass which sublimes in white shining tables. It deliquesces on exposure, and its solution may be obtained by dissolving the hydroxide in hydrochloric acid. The strongly concentrated solution solidifies to a fibrous crystalline mass, which on heating emits hydrochloric acid. It forms with the chlorides of the alkali metals easily soluble double salts, as $KCl + 2ThCl_4 + 18H_2O$.

Thorium Fluoride, ThF_4, is obtained in the form of a heavy white insoluble powder by dissolving the hydroxide in hydro-

[1] Cleve, *Bull. Soc. Chim.* N.S. xxi. 115.

fluoric acid and evaporating to dryness. If a solution of a thorium salt be precipitated by a soluble fluoride, a gelatinous precipitate of $ThF_4 + 4H_2O$ is thrown down.

Potassium Thorofluoride, $K_2ThF_6 + 4H_2O$, is obtained by boiling the hydroxide with potassium fluoride and hydrofluoric acid, in the form of a heavy black powder. When a solution of the chloride is precipitated with acid potassium fluoride the compound $K_2ThF_6 + 4ThF_4 + H_2O$ is thrown down.

Thorium Sulphate, $Th(SO_4)_2$, is obtained by dissolving the oxide in hot concentrated sulphuric acid, or by rubbing up powdered thorite or orangeite to a paste with sulphuric acid, and heating the mixture to 500° until all the excess of sulphuric acid is driven off. The mass is then treated with cold water and boiled, when a crystalline precipitate of $2\,Th(SO_4)_2 + 9H_2O$ remains, and this may be purified by repeated solution in cold water and reprecipitation on boiling. If the solution be allowed to evaporate at the ordinary temperature, transparent monoclinic crystals of $Th(SO_4)_2 + 9H_2O$ are deposited. Thorium sulphate forms double salts with the sulphates of the alkali metals. $Th(SO_4)_2 + K_2SO_4 + H_2O$ crystallizes in four-sided prisms, which are easily soluble in water, but do not dissolve in a solution of potassium sulphate.

Thorium Nitrate, $Th(NO_3)_4 + 12H_2O$, is a very soluble salt, crystallizing in large tables.

The *phosphate* is a precipitate insoluble both in water and phosphoric acid.

Thorium Sulphide, ThS_2. The metal burns in sulphur vapour with great brilliancy, forming a yellow powder, which exhibits a metallic lustre under the burnisher (Berzelius). When the oxide is heated in a current of hydrogen and carbon disulphide vapour, the sulphide is obtained as a black mass, which on rubbing assumes a metallic lustre. It is insoluble in hydrochloric acid, is only slowly attacked by nitric acid, but dissolves easily in aqua regia (Chydenius).

Detection and Estimation of Thorium.

514 The compounds of this metal give no characteristic blowpipe- or flame-reaction. The alkalis and ammonium sulphide precipitate from its solutions the hydroxide insoluble in excess, and the carbonates give rise to a precipitate of a basic carbonate, which dissolves in an excess of the reagent. Ammonia produces

no precipitate in this solution as it does in the corresponding one containing zirconium. Another characteristic property of thorium is its reaction with potassium sulphate, and especially the fact that the thiosulphate is thrown down from thorium solutions on addition of potassium thiosulphate, a reaction by which this metal may be separated from the metals of the cerium group. In order to separate it from titanium, niobium and tantalum, ammonium oxalate is added to the solution, when the thorium alone is precipitated. Thorium can be separated from zirconium by throwing down both metals as oxalates by ammonium oxalate, and then adding an excess of oxalic acid when the zirconium oxalate dissolves completely, leaving behind the oxalate of thorium. Thorium is determined quantitatively as the oxide obtained by igniting the precipitated hydroxide.

The *atomic weight* of thorium has been determined by several chemists without concordant results. Thus Berzelius[1] makes it 236·7, whilst Delafontaine[2] finds the number 230·9 as the mean of several well-agreeing analyses of the sulphate. Cleve, by the same method, obtained the number 233·2, whilst analyses of the oxalate yielded him the number 233·4.

[1] *Pogg. Ann.* xvi. 385.

[2] *N. Arch. Ph. Nat.* xviii. 343.

METALS OF THE ANTIMONY GROUP.

Vanadium.	Tantalum.
Antimony.	Niobium.
Bismuth.	

515 THE members of this group of metals are closely connected with the elements of the Nitrogen Group, resembling these especially in their power of giving rise to acid-forming pentoxides.

VANADIUM, V = 51·2.

In 1801, Del Rio pointed out the existence of a new metal in a lead ore found at Zimapan, in Mexico,[1] and gave to it the name Erythronium, from the fact that its salts became red when heated with acids. In 1805, Collet-Descotils expressed his opinion that this supposed new metal was an impure oxide of chromium, and Del Rio accepted this conclusion as correct. In 1830, Sefström[2] described a new metal which he found in the celebrated iron of Taberg, and for this he proposed the name of Vanadium, from *Vanadis*, a cognomen of the Scandinavian goddess Freia. Whilst in the same year Wöhler[3] showed that Del Rio's discovery was a true one, and that the Zimapan ore is a vanadate of lead. Unable to carry out the further investigation of the new metal, Sefström handed the materials, amounting only to a few grams, to Berzelius, and in 1831 this chemist[4] published the results of an exhaustive investigation on the subject, describing a large number of vanadium compounds, and came to the conclusion that vanadium closely resembles chromium and molybdenum, yielding, like these metals, an acid-

[1] *Gilbert's Ann.* lxxi. 7.
[2] *Pogg. Ann.* xxi. 48.
[3] *Pogg. Ann.* xxii. 1.
[4] Ibid. xxii. 1.

forming trioxide. This view was universally adopted until the year 1867, when Roscoe showed that the substance supposed by Berzelius to be vanadium was, according to the mode of its preparation, either an oxide or a nitride; that the volatile trichloride of Berzelius contains oxygen, and possesses a composition analogous to phosphorus oxychloride; and that the metal, instead of belonging, as was supposed, to the chromium group, is a member of the antimony group and intimately connected with the nitrogen, phosphorus, and arsenic family.

Vanadium is an extremely rare substance, forming an essential constituent of only a few scarce minerals. Traces of this element are, however, tolerably widely distributed throughout terrestrial matter, and it exists in the sun.

The principal vanadium minerals are vanadinite, or lead vanadate, $3Pb_3(VO_4)_2 + PbCl_2$; dechenite, $(PbZn)(VO_3)_2$; descloizite, $Pb_2V_2O_7$; pucherite, $BiVO_4$; psittacinite, $(PbCu)_3(VO_4)_2 + 3Cu(OH)_2 + 6H_2O$; volborthite, $(CuCa)_3(VO_4)_2 + H_2O$; roscoelite, $4AlVO_4 + K_4Si_9O_{20} + H_2O$; mottramite, $(PbCu)_3(VO_4)_2 + 2(PbCu)(OH)_2$. Mottramite has lately been found in tolerable quantity in the copper-bearing beds of the Keuper, worked at Alderley Edge and Mottram St. Andrews in Cheshire, and it is from this source that the vanadic acid of commerce is obtained, it being manufactured on the large scale by the Magnesium Metal Company at Patricroft near Manchester. Traces of vanadium have also been found in a large number of clays, in trap and basalt, in certain iron ores and cast-iron, and also in soda-ash, as well as in phosphate of soda, the latter in one instance containing as much as 0·2 per cent.

Extraction and Preparation of the Vanadium Compounds. The methods adopted for the preparation of vanadium from its various sources depend upon the fact, discovered by Sefström, of the existence of an insoluble ammonium metavanadate, which by repeated crystallization can be obtained free from phosphorus and other impurities.

In order to prepare vanadium salts from mottramite, the keuper-sandstone, which contains the mineral deposited as a film on the surface of the grains of sand, is digested with strong hydrochloric acid, the acid liquor drawn off and the sand well washed with water. The acid solution, together with the washings, after concentration, is evaporated down with an excess of sal-ammoniac, when metavanadate of ammonia separates out, and this is repeatedly crystallized to free it from

copper and iron. The crude ammonium metavanadate is then gently roasted in porcelain, by which means the vanadium pentoxide is obtained in a tolerably pure condition. In order to purify this it is suspended in water and ammonia gas passed into the liquid. A solution of ammonium vanadate is thus formed and separated by filtration from the residue containing silica, phosphates, &c., and then crystallized by evaporation in platinum; the pentoxide obtained by several repetitions of this treatment is free from phosphorus.

Another method for obtaining vanadium pentoxide consists in the preparation of the pure oxychloride, which, when decomposed by water, yields the acid as a fine orange-coloured powder. In order to free this from any trace of obstinately adhering silica, it is moistened with sulphuric acid and exposed in a platinum vessel for some days to the action of hydrofluoric acid. After expulsion of sulphuric acid and fusion, fine large transparent crystals of chemically pure vanadium pentoxide are obtained.

516 *Metallic Vanadium.*—Berzelius obtained brilliant metallic scales by heating the oxytrichloride in an atmosphere of ammonia. These do not, however, consist of metallic vanadium, but of vanadium nitride. The only method which has been found possible for obtaining metallic vanadium is the reduction of the dichloride in perfectly pure hydrogen. Although this process appears simple enough, there is no metal more difficult to prepare than vanadium. This arises from the fact that whilst vanadium is stable at the ordinary atmospheric temperatures, it absorbs oxygen at a red-heat with the greatest avidity, so that every trace of air or moisture must be excluded during its preparation. Moreover, the dichloride itself cannot be readily obtained in quantity.

For the purpose of reducing the metal the apparatus shown in Fig. 167 is employed. It consists of a hydrogen generator (A) yielding a stream of hydrogen which can be kept constantly passing through the wash-bottles, day and night for a week at a time, by occasionally adding fresh acid to the upper bottle and drawing off the zinc sulphate solution from the lower bottle by the caoutchouc tubing. The first wash-bottle contains a solution of lead acetate, the second one of silver nitrate, and the three others contain boiled sulphuric acid. In order to remove any trace of oxygen which may have accompanied the hydrogen, arising either from diffusion or from

air absorbed in the dilute acid used, a tube (C D) is attached to the last washing-bottle ; the first portion of this tube contains a quantity of platinum sponge (C) which is heated to redness during the whole time the hydrogen is passing through the

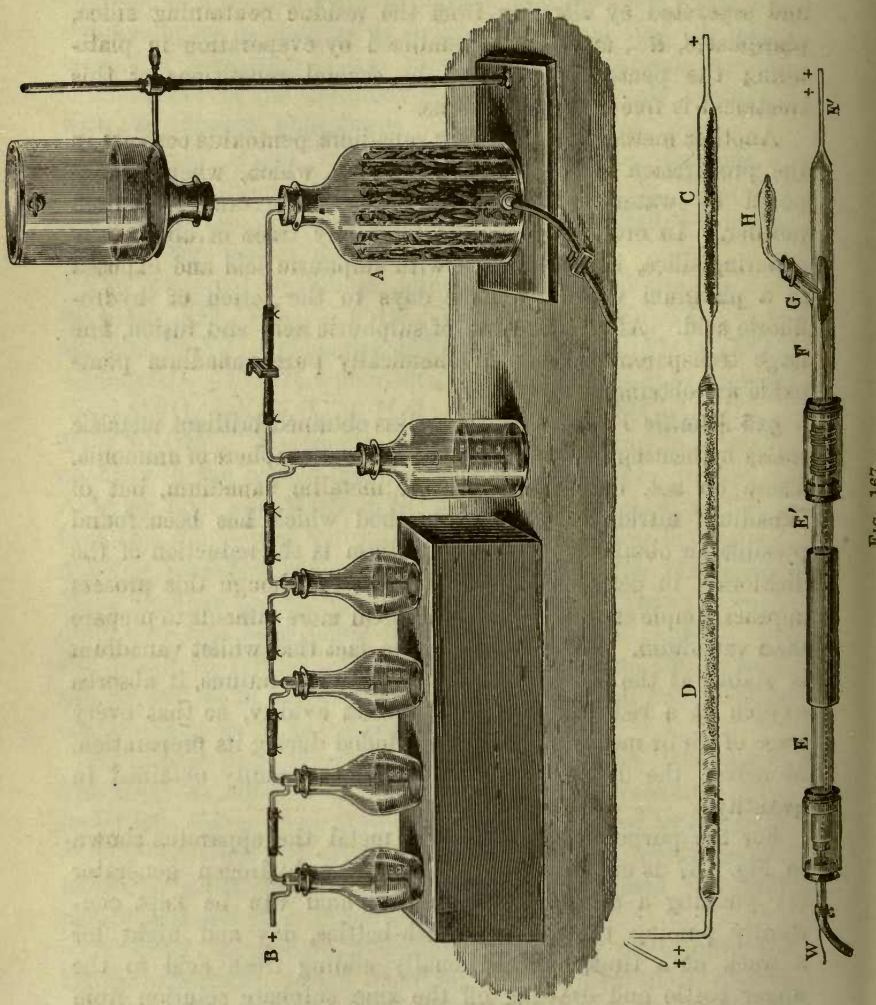

Fig. 167.

apparatus, whilst the further portion of the tube (D) is filled with phosphorus pentoxide and plugs of cotton-wool. The greatest care must be taken to have all caoutchouc stoppers and joints made as tight as possible with copper-wire and paraffin. At right angles to the drying tube (C D) is placed the reducing

arrangement shown in the lower part of the drawing. This consists of a porcelain tube (E E′) placed in a Hofmann's furnace and protected in the central portions, where it is heated, by an outer casing of sheet-iron. The porcelain tube is connected with the hydrogen apparatus by means of the wide glass tube (F F′) provided with the tubulus (G) and narrowed down to join the drying tube at F′. The joint between the porcelain and glass tubes is made of seamless caoutchouc, well wired and covered by an outer short glass cylinder, the space between the tubes and the cylinder being filled either with mercury or fused paraffin, and a similar joint is placed at the further end of the porcelain tube.

The introduction of the anhydrous dichloride without exposure to the air is effected by means of the tubulus (G), the dichloride being contained in the bent tube (H) in which it was prepared and sealed up in hydrogen. After the whole arrangement has been set up, the platinum boat being in position, as shown in the figure, hydrogen is allowed to pass through the apparatus for twelve hours to dry it completely and clear out the air ; the caoutchouc stopper of the tubulus is then withdrawn and the end of the tube containing the dichloride cut off, and the tube and stopper quickly replaced, so that the crystals lie in the horizontal portions of the tube. The bent tube is next so turned in the stopper that the crystals of dichloride fall out and are collected in the platinum boat placed below. This boat, charged with dichloride, is then drawn into the centre of the porcelain tube by means of the platinum wire, the end of which (W) passes tightly through a small hole in the caoutchouc tube at the end of the apparatus. As soon as the boat is in position, the wire is cut off short at the end of the glass tube, a proper joint made, and an exit tube attached dipping under sulphuric acid.

Before the porcelain tube is heated, the caoutchouc stopper of the tubulus is surrounded by a bath of paraffin, and the hydrogen is allowed to bubble through for six hours. The temperature of the porcelain tube is then gradually raised to the highest point (a bright red-heat), which the Hofmann's furnace will yield, and kept constant until the reduction is complete. Torrents of hydrochloric acid gas at once come off, and the process must be continued for some hours after the last trace of acid can be detected in the hydrogen. The process lasts from forty to eighty hours, according as the quantity of dichloride employed varies from 1 to 3 or 4 grams.

Metallic vanadium prepared by reduction from the dichloride in hydrogen is a light whitish-gray coloured powder, which under the microscope reflects light most powerfully, and appears as a brilliant crystalline metallic mass possessing a silver-white lustre. Vanadium thus prepared oxidizes but slowly in the air, nor does it decompose water at the ordinary temperature, and it may be moistened and again dried in a vacuum several times without gaining in weight. Vanadium is neither volatile nor fusible when heated to redness in hydrogen. When the powdered metal is thrown into a flame, or rapidly heated in an excess of oxygen, it burns with brilliant scintillations. The specific gravity of vanadium at 15° is 5·5. The metal is not attacked by hydrochloric acid either when cold or hot, and neither strong nor dilute sulphuric acid act upon the metal in the cold, but when heated with the strong acid the metal slowly dissolves, giving a greenish-yellow solution. Hydrofluoric acid dissolves the metal slowly with evolution of hydrogen and formation of a green solution, whilst nitric acid of all strengths oxidizes it with violence, evolving nitrous fumes and forming a blue liquid. Both hot and cold solutions of caustic soda are without action on the metal, but when fused with the hydroxide, hydrogen is evolved and a vanadate formed.

When heated in an atmosphere of pure nitrogen, metallic vanadium at once absorbs this gas and is converted into the mononitride (Roscoe). It also forms an alloy with platinum.

VANADIUM AND OXYGEN.

517 Vanadium forms five compounds with oxygen, analogous to the oxides of nitrogen, namely:

Vanadium monoxide	V_2O.
Vanadium dioxide, or hypovanadious oxide .	V_2O_2.
Vanadium trioxide, or vanadious oxide . . .	V_2O_3.
Vanadium tetroxide, or hypovanadic oxide . .	V_2O_4.
Vanadium pentoxide, or vanadic oxide . . .	V_2O_5.

All these oxides form salts, the three first acting as basic oxides, the two highest acting as acid-forming oxides. Of these the last oxide is the most important, and it and its compounds will therefore be first described.

Vanadium Pentoxide, V_2O_5. The preparation of this oxide from mottramite has already been described. In the pure state it is best prepared by decomposing the oxychloride, $VOCl_3$, by water and fusing the residue. Vanadium pentoxide crystallizes in splendid yellowish-red rhombic prisms (Nordenskiöld), which have a specific gravity of 3·35 (J. J. Watts), and dissolve in about 1,000 times their weight of water, giving a yellowish solution, which does not possess any taste but turns blue litmus-paper red. Vanadium pentoxide fuses without decomposition in absence of organic reducing matter to a red liquid, which on cooling yields brilliant transparent reddish-yellow needles, and at the moment of crystallization exhibits the phenomenon of incandescence.

Vanadyl Salts. Vanadium pentoxide acts as a weak basic oxide as well as an acid-forming oxide. Thus it dissolves in strong acids, forming red or yellow solutions yielding crystalline compounds, which separate out on spontaneous evaporation or cooling. These are termed the *vanadyl salts*, as they contain the triad radical vanadyl VO.

Vanadyl chloride, $VOCl_3$, is a yellow volatile liquid, which will be hereafter described. No pentachloride of vanadium is known.

Normal Vanadyl Sulphate, $(VO)_2(SO_4)_3$, is obtained, according to Berzelius, by dissolving the pentoxide in hot sulphuric acid which has been diluted with half its weight of water. On evaporating at a low temperature the salt crystallizes out in reddish-brown, very deliquescent scales. The same compound is obtained in ruby-red octohedrons by boiling the pentoxide with an excess of sulphuric acid. When these are heated to the melting-point of lead the basic salt $(VO)_2O(SO_4)_2$ remains as a red mass exhibiting small bright crystalline faces.

If the pentoxide be dissolved in concentrated sulphuric acid and the solution evaporated, the basic salt $VO(OH)SO_4$ is formed[1] as a sandy reddish-yellow powder. According to Gerland this is identical with the preceding compound.

When potassium vanadate is dissolved in strong sulphuric acid and the excess of acid driven off by heat, the double salt $K_2SO_4 + (VO)_2(SO_4)_3$ is obtained as a yellow crystalline powder (Berzelius).

[1] Gerland, *Ber. Deutsch. Chem. Ges.* xi. 98.

VANADIC ACIDS AND THE VANADATES.

518 *Normal Vanadic Acid*, H_3VO_4, is not known.

Metavanadic Acid, HVO_3, was discovered by Gerland.[1] It forms a fine yellow pigment, sometimes termed vanadium bronze, and is employed in place of gold bronze. It is obtained in the form of brilliant scales of a golden or orange colour by boiling aqueous sulphurous acid with copper vanadate, prepared by the double decomposition of ammonium metavanadate and copper sulphate. On boiling this salt for a long time with sulphurous acid a mixture of brown and orange-yellow crystals is obtained, and on continuing the ebullition with more sulphurous acid, the brown crystals dissolve, the yellow metavanadic acid being insoluble.

Vanadium bronze may also be prepared by adding a solution of ammonium vanadate to one of copper sulphate containing excess of sal-ammoniac until a permanent precipitate is formed, and then gently heating to 75°, when the yellow scales are slowly deposited, and after a lapse of a few hours nearly the whole of the vanadium is precipitated. The larger the quantity of material employed and the slower the action takes place, the finer is the colour of the bronze.[2]

If the freshly prepared solution of copper vanadate be quickly evaporated in a flat dish, a crystalline residue is obtained which is soluble in water, and when this solution is dialyzed for some days a clear solution of pure vanadic acid is obtained which remains clear when heated, and deposits the red amorphous pentoxide on evaporation.

Pyrovanadic Acid, $H_4V_2O_7$, is a brown precipitate closely resembling ferric hydrate, obtained by treating a solution of an acid vanadate with nitric acid. When air-dried it possesses the above composition. It is however unstable and loses half its water when dried over sulphuric acid (v. Hauer).

519 *The Vanadates.* Inasmuch as Berzelius thought that vanadium dioxide was the metal, and, therefore, considered the highest oxide to be a trioxide, he likewise assumed that the vanadates corresponded to the chromates. In addition to the so-called normal salts examined by him, two other series were described

[1] *Proc. Manch. Lit. and Phil. Soc.*, 1873, p. 50.
[2] *Ber. Deutsch. Chem. Ges.* ix. 874.

by v. Hauer,[1] which, appearing to correspond to the dichromates and trichromates, received names analogous to these. After the true formula of the highest oxide of vanadium had been ascertained to be V_2O_5, it was evident that the so-called normal vanadates corresponded to the metaphosphates, and it was found possible to prepare both the ortho- and pyro-vanadates analogous to the corresponding phosphates, v. Hauer's salts becoming the tetra- and hex-vanadates. Thus we have:

(1) Sodium Metavanadate . . . . . $NaVO_3$.
(2) Sodium Orthovanadate . . . . . Na_3VO_4.
(3) Sodium Pyrovanadate . . . . . $Na_4V_2O_7$.
(4) Sodium Tetravanadate . . . . . $Na_2V_4O_{11}$.
(5) Sodium Hexvanadate . . . . . $Na_2V_6O_{16}$.

Other polyvanadates of more complicated composition have also been described.[2]

Although the first three classes of vanadates correspond in composition to the phosphates, the order of stability of the soluble vanadates in aqueous solution differs remarkably from that of the phosphates, the metavanadates being the most stable and the orthovanadates being the least stable; whereas in the phosphorus series the order of stability is the reverse of this. At a high temperature, on the other hand, the orthovanadate is the most stable, being formed when vanadium pentoxide is fused with an alkaline carbonate, the meta-salt being produced when a solution of an alkaline carbonate is boiled with vanadium pentoxide.

The reaction which serves best to distinguish the ortho- from the meta-vanadates is the colour of the respective copper salts. Copper orthovanadate possesses a blue-green colour, whilst the metavanadate is a light-yellow crystalline powder.

The alkaline pyrovanadates are soluble, and can be readily obtained by fusing one molecule of vanadium pentoxide with two molecules of the carbonate of an alkali-metal dissolving, and crystallizing. They are likewise obtained by the decomposition of an aqueous solution of the corresponding orthovanadate. The pyrovanadates of the heavy metals are usually insoluble in water, and possess properties generally similar to those of the corresponding orthovanadates.

The metavanadates are usually yellow; some of them, es-

[1] *Journ. Prackt. Chem.* lxix. 385, lxxvi. 156. 929, lxxx. 324.
[2] Carnelley, *Chem. Soc. Journ.*, xxvi. 323.

pecially those of the alkaline earths, zinc, cadmium, and lead, are converted into colourless isomeric modifications, either in the solid state under water, in aqueous solution, and especially in the presence of alkaline carbonates. The metavanadates of the alkali-metals are colourless, and on treatment with an acid give rise to anhydro-salts, which have a fine yellowish-red colour. The metavanadates of ammonium, potassium, sodium, barium, and lead, are but sparingly soluble in water. The other metavanadates are more soluble. The following are the properties of the most important members of these three classes of vanadates.

520 *Potassium Metavanadate,* KVO_3, dissolves slowly in cold and readily in hot water, and with difficulty in caustic potash. The solution on evaporation becomes syrupy, and this dries to a white earthy mass, which, when heated, fuses to a yellow liquid. When it is boiled with water and vanadium pentoxide, or fused with the latter, *potassium tetravanadate,* $K_2V_4O_{11} + 3H_2O$, is obtained, crystallizing in broad reddish-yellow tablets. This salt is slightly soluble in cold and very easily soluble in hot water. On heating it first loses water, becoming of a dull-red colour, and then melts to form a transparent liquid, which solidifies to a yellow mass.

Sodium Orthovanadate, $Na_3VO_4 + 16H_2O$. In order to obtain this salt vanadium pentoxide and carbonate of soda are fused together in the proper proportions. The fused mass is dissolved in the smallest quantity of cold water and a layer of alcohol poured on it, when, after several hours' standing, the salt separates out in colourless needles. It has a strongly alkaline reaction, and is slowly decomposed by water in the cold, and more quickly on boiling into caustic soda and sodium pyrovanadate:

$$2Na_3VO_4 + H_2O = Na_4V_2O_7 + 2NaOH.$$

Sodium Pyrovanadate, $Na_4V_2O_7 + 18H_2O$, crystallizes in large six-sided tables, is easily soluble in water, and is precipitated by alcohol from its aqueous solution in pearly scales. It is best prepared by fusing the pentoxide with the requisite quantity of carbonate of soda. It fuses more easily than the orthovanadate and is first formed in the preparation of the latter salt. If, therefore, the temperature employed be not sufficiently high the latter salt crystallizes out.

Sodium Metavanadate, $NaVO_3$, resembles the potassium salt, and is converted in a similar manner into *sodium tetravanadate* $Na_2V_4O_{11} + 9H_2O$, crystallizing in beautiful large orange-red

crystals. This salt is only slightly soluble in water, but possesses such powerful colouring properties that 1 part of the salt is sufficient to impart a yellow tint to 200,000 parts of water. It effloresces on exposure to the air, becoming of a reddish-brown tint, and melts at a dark red-heat, solidifying to a dark red amorphous mass.

Ammonium Metavanadate, NH_4VO_3, is the most important vanadate. It is obtained by dissolving the pentoxide in an excess of ammonia and evaporating, or by precipitating with alcohol, in which it is insoluble. It forms colourless transparent crystalline crusts, and is insoluble in concentrated solution of sal-ammoniac, and accordingly is precipitated when a lump of sal-ammoniac is allowed to remain in a solution of metavanadate or pyrovanadate :

$$Na_4V_2O_7 + 4NH_4Cl = 2NH_4VO_3 + 2NH_3 + H_2O + 4NaCl.$$

The solution of this salt becomes of a deep black tint when treated with tincture of galls, and Berzelius originally suggested the use of this liquid as an ink. This ink is, however, not permanent, for letters thus written by Berzelius are now quite illegible (Wöhler).

Ammonium Tetravanadate, $(NH_4)_2V_4O_{11} + 4H_2O$, is obtained by addition of acetic acid to a boiling solution of the metavanadate until the precipitate redissolves. The salt separates out from the yellowish-red liquid on cooling in large transparent orange-red crystals. If it be recrystallized from water containing acetic acid, splendid red crystals of the *ammonium hexvanadate* $(NH_4)V_6O_{16} + 6H_2O$, are obtained.

521 *Calcium Pyrovanadate,* $2Ca_2V_2O_7 + 5H_2O$, is a white amorphous precipitate obtained by double decomposition of the corresponding sodium salt with calcium chloride. If the solution of sodium orthovanadate be precipitated by calcium chloride, the same salt is obtained mixed with calcium hydroxide, the orthovanadate being at once decomposed according to the equation :

$$Ca_3(VO_4)_2 + H_2O = Ca_2V_2O_7 + Ca(OH)_2.$$

Lead Orthovanadate, $Pb_3(VO_4)_2$, is a nearly white insoluble precipitate obtained by adding a solution of acetate of lead to one of sodium orthovanadate. This salt occurs in nature combined with lead chloride as vanadinite, $3Pb_3(VO_4)_2 + PbCl_2$ or $Pb_3(VO_4)_2 + Pb_2(VO_4)Cl$. This mineral crystallizes in hexagonal prisms, having a reddish-brown colour, and being isomorphous

with apatite. It has a specific gravity of from 6·6 to 7·2, and frequently contains some phosphoric acid. It was found by Del Rio in Zimapan in Mexico, and occurs also at Leadhills in Scotland, in Carinthia, and in the Urals. It may be obtained artificially by fusing together lead oxide, vanadium pentoxide, and lead chloride, in the right proportions. The fused mass contains druses, in which thin needle-shaped crystals are contained. If boiled with water it falls to a crystalline powder consisting of microscopic hexagonal prisms, possessing the waxy lustre and the yellowish colour of natural vanadinite and having a specific gravity of 6·7 (Roscoe).

Lead Pyrovanadate, $Pb_2V_2O_7$, is found in South America as descloizite in rhombic crystals, which have an orange-green or black colour, a bronze-like lustre, and a specific gravity of 5·839. It usually contains zinc, iron, manganese, and copper as impurities. If a solution of sodium pyrovanadate is precipitated with acetate of lead, the basic salt $Pb_5V_4O_{15}$ is thrown down as a light-yellow precipitate.

Lead Metavanadate, $Pb(VO_3)_2$, is obtained as a yellow precipitate when a solution of a metavanadate is mixed with one of lead acetate. The mineral dechenite chiefly consists of this compound, a portion of the lead however being usually replaced by zinc. It occurs together with lead ores, forming yellow, brown, or deep-red reniform masses, having a specific gravity of 5·6 to 5·8.

Lead Tetravanadate, $Pb_2V_4O_{11}$, is obtained by precipitating the corresponding potassium salt with lead nitrate, in the form of a reddish-yellow precipitate slightly soluble in water.

Copper Orthovanadate, $Cu_3(VO_4)_2 + H_2O$, occurs as the mineral volborthite, in which a part of the copper is replaced by calcium; it crystallizes in small yellow or green hexagonal tables, having a specific gravity of 3·55, and is found in Thuringia and in the Urals.

Copper Pyrovanadate, $Cu_2V_2O_7$, is a yellow crystalline precipitate, whilst *copper metavanadate* is an apple-green precipitate.

Silver Orthovanadate, Ag_3VO_4, is obtained by precipitating a freshly prepared solution of the sodium salt with silver nitrate. It is a deep orange-red coloured precipitate, which is easily soluble in nitric acid and in ammonia.

Silver Pyrovanadate, $Ag_4V_2O_7$, is a heavy yellow powder.

Silver Metavanadate, $AgVO_3$, forms a pale yellow gelatinous precipitate.

THE LOWER OXIDES OF VANADIUM AND THEIR COMPOUNDS.

522 *Vanadium Monoxide*, V_2O, is formed by the prolonged exposure of metallic vanadium to the air. It is a brown substance, which, when heated in the air, is gradually converted into the higher oxides. No salts of this oxide have been prepared.

Vanadium Dioxide, or *Hypovanadious Oxide*, V_2O_2, in its power of uniting with oxygen vanadium even surpasses uranium,[1] and, like uranium, it can only be separated from its last portions of oxygen with extreme difficulty. The oxide V_2O_2 is, moreover, found to enter as a radical into many compounds, so that the name vanadyl (VO) may appropriately be given to it. This substance, which was regarded by Berzelius as metallic vanadium, may be prepared by reducing the higher oxides by potassium, or by passing the vapour of vanadyl trichloride, $VOCl_3$, mixed with excess of hydrogen, through a combustion tube containing red-hot carbon.[2] Thus obtained it forms a light-grey glistening powder or a lustrous metal-like crust, having a specific gravity of 3·54. It is brittle, difficultly fusible, and conducts electricity. Heated to redness, it takes fire in the air and burns to the trioxide V_2O_3, whilst when heated in chlorine the oxychloride $VOCl_3$ is formed. It is insoluble in sulphuric, hydrochloric, and hydrofluoric acids, but dissolves easily in aqua regia, yielding a blue liquid. Although vanadium dioxide does not dissolve in acids, it can be obtained in solution, yielding the hypovanadious salts. These are obtained by the action of nascent hydrogen, evolved by metallic zinc, cadmium, or sodium-amalgam, upon a solution of vanadium pentoxide in sulphuric acid. The liquid rapidly changes colour, passing through all shades of blue and green until after some time it assumes a permanent lavender or violet tint. In order to prove that this solution really contains the vanadium in the state of dioxide, a standard solution of potassium permanganate is added until a permanent pink colour is obtained and the vanadium has reached the highest degree of oxidation, when it is found that for every two atoms of metal three atoms of oxygen have been added. This solution of hypovanadious sulphate absorbs oxygen with

[1] Peligot, *Ann. Chim. Phys.* [3], v. and xii.
[2] Schafarik, *Ann. Chem. Pharm.* cix. 85.

such avidity as to bleach indigo and other vegetable colouring matters as quickly as chlorine. On allowing the neutralized lavender-coloured solution to stand exposed to the air for a few seconds, the colour changes to a deep chocolate-brown: and so rapid is the alteration of colour when but little free acid is present that such a lavender solution may serve as a reagent for the detection of free oxygen not inferior in delicacy to an alkaline pyrogallate. The changes in colour which the yellow sulphuric acid solution of vanadium pentoxide undergoes on reduction are exceedingly characteristic, and may be divided into eight stages, as follows:

Stage.	Colour.	Reaction.	State of Oxidation of the Metal.
I.	Yellow	Acid	Vanadic oxide.
II.	Green	Acid	Vanadic to hypovanadic oxide.
III.	Bluish-Green	Acid	Vanadic to hypovanadic oxide.
IV.	Blue	Acid	Hypovanadic oxide.
V.	Greenish-blue	Acid	Hypovanadic to vanadious oxide.
VI.	Green	Bleaches slightly	Vanadious to hypovanadious oxide.
VII.	Bluish-violet	Bleaches strongly	Vanadious to hypovanadious oxide.
VIII.	Lavender or violet	Bleaches strongly	Hypovanadious oxide.

Thus vanadic salts are yellow; the hypovanadic salts blue; the vanadious salts green; and the hypovanadious salts lavender-coloured.

Vanadium Trioxide or *Vanadious Oxide*, V_2O_3, is obtained by heating the pentoxide in hydrogen, or by igniting the same oxide in a carbon crucible. It is a black powder, which may by pressure be united to form a coherent mass which conducts electricity. It undergoes oxidation when exposed to the air, not only being pyrophoric when warm, but also slowly taking up oxygen when exposed to the air at ordinary temperatures, and being converted into small dark indigo-coloured crystals of the tetroxide. It has a specific gravity of 4·7. When ignited in chlorine gas it is converted into vanadyl chloride $VOCl_3$, and vanadium pentoxide:

$$3V_2O_3 + 6Cl_2 = V_2O_5 + 4VOCl_3.$$

It is insoluble in most acids, but it may be obtained in solution by the reducing action of nascent hydrogen, evolved from metallic magnesium, on a solution of vanadium pentoxide in sulphuric acid. A green liquid is thus obtained, the further reduction observed in the case of zinc, cadmium, and sodium-amalgam not taking place in the case of magnesium. The green solution may likewise be obtained by the partial oxidation of the lavender-coloured solution of hypovanadious oxide. If a current of air be passed through such a solution, in which the free acid has been neutralized by an excess of zinc and the remaining metallic zinc removed, the liquid attains a permanent brown colour, which on the addition of a few drops of acid turns green and the solution now contains vanadious sulphate. The vanadious salts have not been fully examined.

Vanadium Tetroxide, or *Hypovanadic Oxide*, V_2O_4. This oxide can be prepared either by the oxidation of the dioxide in the air, or by the partial reduction of the pentoxide. It dissolves in acids, forming solutions of the hypovanadic salts, which possess a bright blue colour. Solutions of these salts are also produced by the action of moderate reducing agents, such as sulphur dioxide and sulphuretted hydrogen or oxalic acid upon solutions of vanadic acid in sulphuric acid. Also by passing a current of air through acid solutions of the hypovanadious salts until a permanent blue colour is attained.

Hypovanadic or Divanadyl Compounds.

523 These may be considered as containing the tetravalent radical divanadyl, V_2O_2.

Hypovanadic Hydroxide, $V_2O_4.7H_2O$ or $V_2O_2(OH)_4 + 5H_2O$, forms a grayish-white precipitate, obtained when a solution of hypovanadic sulphate or chloride is cautiously precipitated with a cold solution of sodium carbonate. When dried it is a black amorphous mass, having a glassy fracture. This on heating to 100° loses four molecules of water, leaving the hydrate $V_2O_4 + 3H_2O$. Hypovanadic oxide acts both as a basic and as an acid-forming oxide. When dissolved in acids the hypovanadic salts are formed, whilst with alkalis the hypovanadates are produced.

Hypovanadic Tetrachloride, $V_2O_2Cl_4 + 5H_2O$. When vanadium pentoxide is dissolved in hot concentrated hydrochloric acid, chlorine is evolved and a green solution is obtained, which

becomes blue with deposition of sulphur when sulphuretted hydrogen is passed through the liquid. A brown amorphous deliquescent mass is obtained on evaporation, possessing the above composition. It dissolves in water, yielding a blue solution; but when treated with strong hydrochloric acid or alcohol the solution is brown, and this change is explained by the existence of two different hydrates. On ignition in a current of carbon dioxide it decomposes as follows:

$$V_2O_2Cl_4 + 5H_2O = V_2O_4 + 4HCl + 3H_2O.$$

The tetroxide thus obtained is amorphous and has a greenish tint, owing to the presence of a small quantity of pentoxide.[1]

Hypovanadic Sulphate, $V_2O_2(SO_4)_2$, is deposited as a greenish-blue sandy powder by dissolving the tetroxide in excess of sulphuric acid and heating the solution for some time to the boiling-point of the acid.[2] If the tetroxide be dissolved in sulphuric acid, the solution evaporated, and the residue treated with absolute alcohol, a sky-blue powder remains, which deliquesces in moist air. If the solution be allowed to evaporate spontaneously over sulphuric acid, fine blue rhombic prisms having the composition $V_2O_2(SO_4)_2 + 4H_2O$ are deposited (Berzelius). An acid salt, $V_2O_2SO_4(SO_4H)_2 + 5H_2O$, is prepared by evaporating the sulphuric acid solution of the trioxide, drying the crystals on a porous plate, and then washing them with ether (Crow); and a similar salt, $V_2O_2SO_4(SO_4H)_2 + 3H_2O$, is obtained by precipitating a concentrated solution of any of the hypovanadic sulphates with concentrated sulphuric acid. Other hydrates and double salts of this series are also known; the composition of these compounds will be found in the memoirs above referred to.

The remaining hypovanadic salts have been but incompletely studied. Certain of them have been described by Berzelius and more recently by Guyard.[3]

The *hypovanadates* are all insoluble except those of the alkali metals. The alkaline hypovanadates are obtained by adding an excess of caustic alkali to a concentrated solution of hypovanadic sulphate. The dark-brown solution thus obtained with potash deposits *potassium hypovanadate*, $K_2V_4O_9 + 7H_2O$, in reddish-brown crystalline scales, which, after washing first

[1] Crow, *Journ. Chem. Soc.* 1876, ii. 453.
[2] Gerland, *Ber. Deutsch. Chem. Ges.* x. 2109.
[3] *Bull. Soc. Chim.* [2], xxv. 350.

with potash solution, and then with alcohol, may be dried between filter-paper. This salt is permanent in the air, and very soluble in water, yielding a dark-brown solution.

Sodium Hypovanadate, $Na_2V_4O_9 + 7H_2O$, is prepared in a similar way to the potassium salt and exhibits analogous properties.

Ammonium Hypovanadate, $(NH_4)_2V_4O_9 + 3H_2O$, is obtained as a dark-brown crystalline precipitate by adding a hypovanadic sulphate solution to ammonia; it dissolves in water, yielding an almost black solution (Crow).

The hypovanadates of the heavy metals are insoluble precipitates.

Lead Hypovanadate, PbV_2O_5, is precipitated when a solution of lead acetate is added to a solution of potassium hypovanadate.

Silver Hypovanadate, $Ag_2V_2O_5$, is a black crystalline powder formed according to the following equation:

$$K_2V_4O_9 + 4AgNO_3 + H_2O = 2Ag_2V_2O_5 + 2KNO_3 + 2HNO_3.$$

VANADIUM AND CHLORINE.

524 The only compounds of vanadium and chlorine described before 1867 were oxychlorides. Three chlorides free from oxygen have been subsequently obtained either by the action of chlorine or the nitride of vanadium, VN, or by distilling the oxychlorides over charcoal.[1] The following chlorides and oxychlorides of vanadium are known:

Chlorides.

Vanadium tetrachloride	VCl_4.
,, trichloride .	VCl_3 or V_2Cl_6.
,, dichloride .	VCl_2 or V_2Cl_4.

Oxychlorides.

Vanadyl trichloride . .	$VOCl_3$.
,, dichloride . .	$VOCl_2$.
,, monochloride .	VOCl.
Divanadyl monochloride	V_2O_2Cl.

[1] Roscoe, *Phil. Trans.* 1869, 678.

Vanadium Tetrachloride, VCl_4, is formed when metallic vanadium or the mononitride is heated to redness in an excess of chlorine. It is best prepared by repeatedly passing the vapour of vanadium oxychloride, together with an excess of dry chlorine, over a long column of pure sugar-charcoal heated to a dull redness. Vanadium tetrachloride is a dark brownish-red thickish liquid, which evolves white fumes when exposed to moist air. It boils at 154° with partial decomposition, losing chlorine and leaving a residue of the sesquichloride. This decomposition also takes place at the ordinary temperature, especially on exposure to light. It does not solidify at —18°; its specific gravity at 0° is 1·8584, and the specific gravity of its vapour is 6·69, the calculated specific gravity being 6·675. When thrown into water the tetrachloride is at once decomposed, yielding a blue solution of hypovanadic chloride.

The tetrachloride heated in excess of either chlorine or bromine splits up into trichloride and free chlorine, so that vanadium does not appear to form a penta-compound with the chlorous elements.

Vanadium Trichloride, V_2Cl_6. The foregoing compound easily decomposes, as has been stated, into this body and chlorine. The trichloride is obtained either by the slow decomposition of the tetrachloride at the ordinary temperature or at its boiling-point, or, together with the dichloride, when the vapour of the tetrachloride mixed with hydrogen is passed through a red-hot tube. It is a solid substance, crystallizing in fine peach-blossom coloured, shining tables, closely resembling in appearance the crystals of chromium sesquichloride. It is non-volatile when heated in hydrogen, and decomposes when heated in the air. Ignited in a current of hydrogen, it first loses one atom of chlorine, forming the dichloride VCl_2, parting at a higher temperature with the whole of its chlorine, and leaving a residue of metallic vanadium as a lustrous gray powder. It is extremely hygroscopic, instantly deliquescing on exposure to moist air to a dark-brown liquid, which on addition of a drop of hydrochloric acid becomes green, forming a solution of vanadious chloride. The specific gravity of vanadium trichloride is 3·0; it readily dissolves in absolute alcohol and in ether, forming green-coloured solutions.

Vanadium Dichloride, VCl_2. This is a solid body, crystallizing in fine apple-green coloured plates, having a micaceous lustre and an hexagonal form. It is prepared by passing the vanadium tetrachloride, mixed with dry and pure hydrogen,

through a glass tube heated to dull redness. Its specific gravity at 18° is 3·23. It is very deliquescent, yielding a lavender-coloured solution of hypovanadious chloride, which possesses bleaching properties. When the dichloride is heated to whiteness in a current of dry ammonia, vanadium mononitride is obtained in bronze-coloured pseudomorph crystals.

525 *Vanadium Oxychloride*, or *Vanadyl Trichloride*, $VOCl_3$. This compound, corresponding to phosphorus oxychloride, is obtained either by the action of chlorine on the oxide V_2O_3 as already described, or by heating a mixture of the pentoxide and charcoal in a current of chlorine:

$$V_2O_5 + 3C + 3Cl_2 = 2VOCl_3 + 3CO.$$

In the latter case the resulting liquid is red-coloured from presence of tetrachloride, and is best purified by rectification over clean sodium in a current of carbon dioxide. Vanadyl trichloride thus obtained is a bright lemon-yellow coloured mobile liquid, boiling at 126°·7 and having a specific gravity at 14° of 1·841. It does not solidify at —15°. The specific gravity of its vapour is 6·108, the calculated specific gravity being 6·003.

On exposure to moist air vanadyl trichloride emits vapours of a cinnabar-red colour, and is soon decomposed in the presence of moisture into vanadic and hydrochloric acids. When a small quantity of water is added it becomes thick and blood-red coloured, owing to the formation of vanadic acid. A large quantity of water, however, yields a clear yellow solution. When the oxychloride is ignited in a current of dry ammonia gas, vanadium mononitride is obtained. Vanadium trichloride combines with ether at 70°, forming a compound crystallizing in long red needles, having the composition $VCl_3(OC_2H_5)_2$, therefore corresponding to the pentachloride, in which two atoms of chlorine are replaced by two molecules of oxethyl.[1]

When vanadium oxychloride is heated with zinc to 400°, vanadium dioxide and *vanadyl dichloride* $VOCl_2$, are formed; the latter crystallizes in green tables which deliquesce on exposure to moist air. The same compound is formed when the vapour of vanadyl trichloride and hydrogen are passed through a red-hot tube. In this case both *vanadyl monochloride* VOCl, and *divanadyl monochloride*, V_2O_2Cl, are likewise formed, the

[1] Bedson, *Chem. Soc. Journ.* 1876, i. p. 309.

former as a flocculent brown powder insoluble in water, and the latter in the form of a yellow crystalline powder resembling mosaic gold. The molecular formulæ of these bodies is not known.

VANADIUM AND BROMINE.

526 *Vanadium Tribromide*, VBr_3. This is the only known compound of the above elements. It condenses as a grayish-black compact amorphous sublimate, when dry bromine vapour is passed in excess over vanadium nitride, or over a mixture of vanadium trioxide and charcoal heated to redness. It is a very unstable compound, losing bromine even at the ordinary temperature in dry air, and deliquescing rapidly on exposure to moist air.

Vananyl Tribromide, $VOBr_3$, obtained by passing dry bromine vapour over vanadium trioxide heated to redness, is a dark-red transparent liquid, having a density of 2·967 at 0°. It may be distilled under diminished pressure, passing over without decomposition, at a temperature of about 130° under a pressure of 100 m.m. When heated under the ordinary atmospheric pressure it suddenly solidifies at 180°, decomposing into *vanadyl dibromide*, $VOBr_2$, and free bromine. The latter oxybromide can be obtained directly by dissolving vanadium tetroxide in hydrobromic acid:

$$V_2O_4 + 4HBr = 2VOBr_2 + 2H_2O.$$

No compounds of *vanadium* and *iodine* are known.

VANADIUM AND FLUORINE.

527 Neither a fluoride nor an oxyfluoride of vanadium is known, but a series of fluoxyvanadates have recently been described by Baker.[1]

Potassium Fluoxyvanadates. Vanadium pentoxide easily dissolves in a solution of hydrogen potassium fluoride with evolution of heat, and on cooling yellowish globular masses separate out, consisting of pearly, probably hexagonal, crystals, which have the composition $6KF.V_2O_5.2VOF_3 + 2H_2O$. The

[1] *Journ. Chem. Soc.* 1878, ii. 338.

aqueous solution is yellow and possesses an acid reaction; the dry salt does not smell of hydrofluoric acid, and attacks glass only slowly. When this salt is dissolved in warm hydrofluoric acid, the compound $3KHF_2.2VOF_3$ is obtained in almost colourless tufts of needles, which when dry smell of hydrofluoric acid and attack glass.

Ammonium Fluoxyvanadates. When the pentoxide is dissolved in ammonium fluoride no salt separates out on standing, but if more of the last-named salt be added the compound, $6NH_4F.V_2O_5.2VOF_3 + 2H_2O$, crystallizes out in light-yellow, pearly, hexagonal scales. On solution in water and addition of more hydrogen ammonium fluoride, a fine yellow crystalline salt, $12NH_4F.V_2O_5.2VOF_3$, is precipitated in microscopic pyramids, and this dissolved in hydrofluoric acid, yields the compound, $3NH_4HF_2.2VOF_3$, corresponding to one of the potassium salts. If sulphuretted hydrogen be passed into a solution of the pentoxide in hydrofluoric acid and the resulting blue solution evaporated and ammonium fluoride added to the concentrated liquid, transparent blue monoclinic prisms of *ammonium fluoxyhypovanadate*, $2NH_4F.VOF + H_2O$, are deposited. *Zinc fluoxyvanadate*, $Zn_2OF_2.2VOF_3 + 14H_2O$, is formed by dissolving zinc carbonate and vanadium pentoxide in hydrofluoric acid. The salt crystallizes in hard, yellow, monoclinic prisms.

VANADIUM AND SULPHUR.

528 Two sulphides of vanadium are known corresponding to the tetroxide and pentoxide. These both act as acid-forming sulphides, giving soluble salts with the alkaline sulphides.

Vanadium Tetrasulphide, V_2S_4, is a black compound formed by heating the tetroxide to redness in a current of sulphuretted hydrogen, or in the form of a hydrate, by acidifying the purple-brown solution of a *hypothiovanadate* obtained by dissolving a hypovanadic salt in an excess of an alkaline monosulphide; on drying it yields a black mass.

Vanadium Pentasulphide, V_2S_5, is obtained as a hydrated precipitate when a vanadate is dissolved in an alkaline sulphide and hydrochloric acid added. It resembles the foregoing compound and forms with basic metallic sulphide salts, termed the *thiovanadates*, some of which are crystalline (Berzelius).

VANADIUM AND NITROGEN.

529 *Vanadium Mononitride*, VN. The process described by Berzelius for preparing metallic vanadium by heating the ammonio-oxychloride in an atmosphere of ammonia does not yield the metal, but the mononitride, vanadium being distinguished from most other metals by its power of direct union with nitrogen. The substance obtained by strongly igniting the ammonio-oxychloride in a current of dry ammonia (or rather of its component gases) at a white heat is a greyish-brown powder, which does not undergo change at ordinary temperatures. The mononitride is likewise obtained when the black residue left on calcining ammonium metavanadate in the air is heated to whiteness in a current of dry ammonia. Another and still more simple plan of obtaining the nitride is to expose the oxide to the action of ammonia gas at a white-heat. It is a singular fact that in the presence of nitrogen and hydrogen the whole of the oxygen should be replaced by nitrogen.

When heated in the air vanadium mononitride glows and slowly oxidizes to the blue oxide.

Vanadium Dinitride, VN_2, is obtained as a black powder by passing ammonia over vanadyl trichloride, heating the residue in a glass tube to expel sal-ammoniac, washing with water, and drying in a vacuum over sulphuric acid.

Detection and Estimation of Vanadium.

530 Insoluble vanadium compounds can be brought into solution either by treatment with acids or with alkalis. The hydrochloric acid solution assumes a bright blue colour on the addition of zinc. A solution of hypovanadic sulphate cannot be distinguished in colour from one of copper sulphate when diluted to the requisite extent with water. It however, of course, does not become colourless in presence of metallic iron. Solutions of certain vanadates also closely resemble solutions of the chromates. Thus, for instance, a solution of the tetravanadate of potassium does not differ in appearance from one of potassium bichromate. They may, however, be distinguished from one another, inasmuch as the vanadate solution becomes blue, whilst the chromate assumes a green colour on deoxidation. When

a solution of vanadic acid or an acid solution of an alkaline vanadate is shaken up with ether containing hydrogen peroxide, the aqueous solution assumes a red colour like that of ferric acetate. This reaction serves to detect 1 part of vanadic acid in 40,000 parts of the liquid. Chromic acid does not interfere with the reaction.[1]

For the *quantitative* determination of vanadium, Von Hauer proposed the precipitation of ammonium metavanadate insoluble in solution of sal-ammoniac. This on ignition yields the pure pentoxide. But this separation of vanadic acid from the metals of the alkalis by means of chloride of ammonium gives too low results, both as regards the vanadium and the alkali. It is almost impossible to prevent traces of ammonium metavanadate from dissolving, and on ignition, even with the greatest care, some portions of the finely-divided vanadium pentoxide are invariably carried off when the ammonia escapes. On the other hand, the volatilisation of the comparatively large quantities of sal-ammoniac which must be employed in order to ensure the complete precipitation of the vanadium almost always entails a considerable loss of the fixed alkaline chlorides. A far more accurate plan for the separation of vanadium is the precipitation of the soluble vanadate by acetate of lead, when basic lead vanadate is precipitated, which is so insoluble that a portion when finely powdered and boiled in water does not dissolve in sufficient quantity to enable the lead to be detected in the filtrate by the reaction with sulphuretted hydrogen. The salt is also insoluble in acetic acid, but it dissolves readily in nitric acid, liberating vanadic acid, which separates out, but dissolves completely when the liquid is warmed. In the analysis of a soluble vanadate this insoluble lead salt is collected on a filter, dried at 100° and weighed; a given quantity of the dried salt is then dissolved in nitric acid, the lead precipitated by pure sulphuric acid, and the lead sulphate determined with the usual precautions of evaporation with addition of alcohol, &c. The lead sulphate thus obtained is (contrary to Berzelius's statement) quite free from vanadium, whilst the vanadium pentoxide in the filtrate is obtained perfectly pure and well crystallized on evaporation and ignition. The filtrate from the lead vanadate, freed from excess of lead by means of sulphuric acid and evaporated, yields the alkaline sulphate, not containing a trace of vanadium. Vanadium may be very readily determined volu-

[1] G. Werther, *Journ. Pract. Chem.* lxxxviii. 195.

metrically when no other reducible metals are present. For this purpose the solution of vanadic acid in sulphuric acid is diluted and reduced by passing a current of sulphur dioxide through it and afterwards boiling to expel the excess of this gas. Standard permanganate is then added until a permanent colouration is obtained.

531 The *atomic weight* of vanadium has been determined in two ways. The first is by igniting vanadium pentoxide in dry hydrogen, when it is reduced to the trioxide, and the atomic weight of vanadium is then deduced by the equation—

$$x = 7{\cdot}98\,\frac{(56-3a)}{a-b}$$

where a is the weight of vanadium pentoxide taken, and b is the weight of trioxide obtained.

The following results were obtained by Roscoe :[1]

	Weight of pentoxide taken.	Weight of trioxide obtained.	Atomic weight of vanadium.
(1) . .	7·7397	6·3827	51·13
(2) . .	6·5819	5·4296	51·26
(3) . .	5·1895	4·2819	51·35
(4) . .	5·0450	4·1614	51·22

The mean atomic weight of these four experiments is 51·24, with a mean error of 0·065. Berzelius found as a mean of four experiments that 120·927 parts of pentoxide yielded 100 of the trioxide ; which gives, according to the above equation, $x = 52{\cdot}42$. This difference is probably due to the fact that the vanadium employed by Berzelius contained a trace of phosphorus, which prevented the complete reduction.

The second method for the determination of the atomic weight is the analysis of the vanadyl trichloride. The chlorine in this compound was estimated both by Gay-Lussac's volumetric process and by gravimetric analysis. Nine volumetric determinations gave 61·306 per cent. of chlorine, and eight gravimetric analyses gave 61·241 per cent. of chlorine, the atomic weight from the mean of the seventeen determinations being 51·16. The mean atomic weight of vanadium, according to both methods, is 51·2.

[1] *Phil. Trans.* 1868, 6.

ANTIMONY (STIBIUM) Sb. = 122.

532 This metal occurs in nature chiefly as stibnite or antimony sulphide, Sb_2S_3, a mineral which was known in very early times, having been long employed, as indeed is yet the case, by women in the East for painting the eyebrows. In St. Jerome's translation of the Hebrew of Ezekiel xxiii. 40, we read "circumlinisti stibio oculos tuos;" and in the Second Book of Kings ix. 30 we find, "Porro Jezebel introitu eius audito depixit oculos suos stibio." Of this latter passage Cheyne and Driver give as the translation of the Hebrew "set her eyes in paint (literally antimony)."

The name for this mineral in Hebrew and Arabic is "Kohl," and this word passed as "alcool" or "alkohol" into other languages; thus in the Spanish translation of the Bible the above passage from Ezekiel is thus rendered, "Alcoholaste tus ojos." In the middle ages the word alcohol served to designate any fine powder, and it was only at a later period that it was employed to mean spirits of wine. Dioscorides calls this metal *στίμμι*, and mentions that it is also known by other terms, such as *πλατυόφθαλμον*, the eye-expander, *γυναικείον*, belonging to womankind, &c. Pliny, on the other hand, terms it *stibium*. In the Latin translation of Geber, who also was acquainted with this substance, it is termed *antimonium*, and up to the time of Lavoisier both these words were made use of to signify sulphide of antimony. Spiessglas, the German name for this substance, afterwards changed to spiessglance, is found first in the writings of Basil Valentine, who about the end of the fifteenth century carefully investigated the antimony compounds. In his *Triumphal Car of Antimony* he says: "In order, as is most proper, that I may say something about the name of the material, it should be understood that this material was long known to the Arabians, and from ancient time was termed by them *asinat*. The Chaldeans entitled it *stibium*, and in the Latin tongue it has been called *antimonium*[1] up to the latest times, and in our own German mother tongue the same material has been foolishly

[1] The story of the accidental poisoning of certain monks by spiessglas having given rise to the name of the metal (antimoine) is on the face improbable, and must, as Kopp remarks, have been invented by a Frenchman, whereas Valentine wrote in German!

called spiessglas for this reason, that this material can be fluxed and a glass made from it."

Dioscorides mentions that in order to roast the crude antimony it must be heated in a current of air until it burns, for, if more strongly ignited, it melts like lead. This passage has given rise to the supposition that the author was acquainted with metallic antimony; but this is not the case, for this quotation simply shows that he recognised that spiessglance is a substance that can be readily fused.

The preparation of the metal was first described by Basil Valentine, but not as a new discovery. In his *Wiederholung des Grossen Steins der uralten Weisen* he terms it *spiessglas rex* and also *plumbum antimonii*. It has already been stated that the alchemists considered that each semi-metal was simply a variation of a true metal. In spite of the exact investigations of Basil Valentine, antimony was confounded with bismuth by some chemists, such as Libavius, even so late as the sixteenth century.

Antimony occurs in many other minerals besides stibnite. The metal is found, though not frequently, in the native state, and also as arseniferous antimony or allemontite, As_3Sb_2. Antimony also occurs as the trisulphide, Sb_2S_3, combined with basic sulphides, and in these thioantimonates, a portion of the antimony is usually replaced by arsenic. Amongst such compounds are berthierite, $FeSb_2S_4$; wolfsbergite or antimonial copper, $Cu_2Sb_2S_4$; boulangerite, $PbSb_2S_4$; bleinierite, $Pb_2Sb_2S_5$; bournanite $(Cu_2Pb)_3Sb_2S_6$; freieslebenite, $Ag_{10}Sb_2S_8$; pyrargyrite or red silver ore, $Ag_6Sb_2S_6$, &c. In addition to these we have dyscrasite or antimonial silver, Ag_2Sb; breithauptite or antimonial nickel, NiSb; ullmannite or nickeliferous gray antimony, $Ni(SSbAs)_2$; valentinite or antimony oxide, Sb_2O_3; cervantite or antimony ochre, Sb_2O_4, and stiblithe, $Sb_2O_4 + H_2O$. Antimony is also found in small quantity in iron ores, ferruginous waters, in the coal formation, and in river sand.

533 *Preparation of Metallic Antimony.* The preparation of the metal from the sulphide is a very simple operation. In order to free the ore from quartz or other earthy admixture, the mineral is either melted in vertical cylinders which have a hole at the bottom out of which the molten sulphide drops, or the preliminary fusion is carried on in reverberatory furnaces. The purified sulphide is then either fused with metallic iron, or is roasted in order to convert it into the oxide, and this is reduced with carbon

or with crude tartar. Basil Valentine describes both of these methods in his account of the preparation of the philosopher's stone; he states: "Antimonium is a master in medicine, and from it by means of cream of tartar and salt a King (regulus) is made, steel-iron being added to the spiessglas during fusion. Thus by an artifice a wonderful star is obtained which the learned before my time have termed the philosophical signet star." In the *Triumphal Car of Antimony* he gives the following receipt: "Take good Hungarian spiessglas and with the same quantity of crude tartar, and half as much saltpetre; rub these small and let them fuse well in a wind furnace; afterwards pour out into a mould and allow to cool when a regulus is found."

In order to reduce the oxide obtained by roasting the ore, it is mixed either with 20 per cent. of powdered charcoal which has been saturated with concentrated soda, or with 10 per cent. of crude tartar, and the mixture of ore and reducing agent melted in a large earthen crucible. In this country three operations are necessary for the production of the best star-antimony. The first of these is termed "singling;" in this 40 parts of the sulphide is mixed with about 20 parts of thin scrap iron, and this is then melted in plumbago crucibles, when metallic antimony and iron sulphide are formed. The fusion lasts about an hour and a half, and when complete the charge is poured into conical moulds. The crude metal is then separated from the slag, consisting chiefly of sulphide of iron, which floats on the surface, and it is again melted in the second process of "doubling," with an addition of a small quantity of sodium sulphate and slag obtained in the following operation. The charge for each pot is 80lbs. of crude antimony, 2 lbs. of salt-cake and 2 lbs. of slag, and the fusion lasts about an hour and a quarter. The metal is cast in moulds, allowed to cool, and broken into small pieces ready for the third process, termed "melting for star-metal." For this purpose 2 parts of pearl-ash and 5 parts of slag from a previous operation of the same kind are added to 60 parts of metal and the fusion again repeated. The molten metal is then poured into square moulds in which it is allowed to cool slowly, the surface being at the same time completely covered with slag in order that it may attain the peculiar crystalline structure which is required in commerce. Most of the antimony of commerce is reduced in England, foreign ores, especially those from Borneo, being employed.

It has been already stated that Basil Valentine was acquainted

with the crystalline surface exhibited by pure antimony, but he specially mentions that the regulus which is not starred possesses exactly the same composition as that which presents this peculiarity. He, as well as some of his contemporaries, believed that the stellated surface was only produced when iron was employed in the preparation, whilst other chemists taught that the preparation of the stellated antimony did not depend on the presence of iron, but was connected with a favourable conjunction of the stars. Indeed this latter opinion was pretty generally held until the time of Boyle, who however entirely discredits this explanation, and also states that the starred metal can be obtained without the use of iron.

In his essay *On the Unsuccessfulness of Experiments*, Boyle[1] says: "And it may perhaps also be from some diversity either in antimonies or irons, that eminent chemists have (as we have observed) often failed in their endeavours to make the starry regulus of *Mars* and antimony. Insomuch that divers artists fondly believe and teach (what our experience will not permit us to allow) that there is a certain respect to times and constellations requisite to the producing of this (I confess admirable) body. Upon this subject I must not omit to tell you that a while since an industrious acquaintance of ours was working on an antimony, which unawares to him, was, as we then supposed, of so peculiar a nature, that making a regulus of it alone without iron, the common way (for his manner of operation I inquired of him), he found, to his wonder, and showed me his regulus adorned with a more conspicuous star than I have seen in several stellate reguluses of both antimony and *Mars*."

Lemery, in his *Cours de Chymie*, published in 1675, also argues strongly against the supposition that the planet Mars has anything to do with the formation of the stellated surface.

Commercial antimony often contains traces of arsenic, iron, lead, copper, and frequently some sulphur. In order to prepare the pure metal Liebig's process is the best; this consists in fusing 16 parts of the metal with 2 parts of sodium carbonate, and 1 part of sulphide of antimony for an hour; on cooling, the regulus is separated from the slag, and melted again for an hour with 1½ part of sodium carbonate, and this operation again repeated with 1 part of this salt.[2] According to Schiel[3] a small quantity of nitre should be added from time to time. By

[1] *Opera*, ed. 1772, i. 325. [2] *Liebig's Ann.* civ. 223.
[3] *Ann. Chem. Pharm.* xix. 22.

means of this repeated fusion the whole of the arsenic is separated, provided that a sufficient quantity of iron be originally present in the metal; should this not be the case, it is necessary to add about 2 per cent. of iron sulphide.[1]

Another method of purifying the metal is that described by Wöhler, and improved by Meyer,[2] and this is available when the only impurity present is arsenic. In this process, one part of the metal is ignited with 1·25 parts of sodium nitrate, and 0·5 part of sodium carbonate. The pulverized mass is dissolved in water when pure sodium metantimonate remains behind; this is then reduced by heating with half its weight of cream of tartar or with a mixture of carbon and carbonate of soda.

528 *Properties.* Antimony is a lustrous silver-white metal, which when slowly cooled exhibits a coarsely laminated crystalline fracture. When quickly cooled, on the other hand, the fracture is granular. It crystallizes in obtuse rhombohedrons which can scarcely be distinguished from cubes, and has a specific gravity of 6·71 to 6·86. Native antimony occurs in scaly masses, usually containing silver, iron, and arsenic. Its most important localities are at Sahl in Sweden, Andreasberg in the Harz, Przibram in Bohemia, in the Dauphiny, in Canada, the United States, Mexico, Chili, and at Sarawak in Borneo. Native antimony has a specific gravity of from 6·5 to 7.

Antimony is hard, and so brittle that it can be powdered; it melts at 425°, and volatilizes at a bright red-heat in the air, or in a current of a gas, but not when fused under a layer of common salt. It may be distilled in a current of hydrogen at a white-heat. It does not undergo any alteration on exposure to the air at the ordinary temperature; on heating it burns to form the oxide, and when heated on charcoal before the blowpipe, the oxide is evolved in thick white fumes, and a portion of it is deposited as a white incrustation on the charcoal. If the blast of air be stopped the globule of molten metal begins to glow and is seen to be covered with a crystalline network of needles of oxide, and when the globule is thrown from some height on to a piece of paper, the edges of which are turned up, it breaks into many smaller globules which burn with a very bright flame. Cold water as well as dilute sulphuric acid do not act upon the metal at the ordinary temperature, but at a red-heat it decomposes steam with formation of oxide. It is easily dissolved by hot

[1] Bensch, *Ann. Chem. Pharm.* lxiii. 273.
[2] *Ann. Chem. Pharm.* lxvi. 238.

hydrochloric acid as well as by cold aqua regia, and when heated with concentrated sulphuric acid it is converted into antimony sulphate. Antimony combines directly with the elements of the chlorine group, with those of the sulphur group and with phosphorus and arsenic.

535 *Explosive or Electrolytic Antimony.* This peculiar substance, discovered by Gore,[1] is formed by the union, under certain conditions, of antimony and antimony trichloride. It is obtained by electrolysis of an acid solution of antimony trichloride, having a specific gravity of 1·35, or of a solution obtained by dissolving the trioxide in from 5 to 6 times its weight of hydrochloric acid of specific gravity 1·12, metallic antimony being, in each case, used as the positive, and copper or platinum as the negative pole. The latter becomes covered with a grey lustrous metallic coating, having an amorphous fracture and a specific gravity of 5·78. It contains from 3 to 20 per cent. of antimony chloride, together with a small quantity of free hydrochloric acid. When scratched with a metallic point or touched with a red-hot wire it decomposes with evolution of heat and liberation of the chloride, and when heated to 200° it flies into powder with a loud explosion. If it be prepared under cold water it does not undergo any alteration, but when heated to 75° it decomposes with a hissing sound. Hydrochloric acid is found in solution, and the water becomes turbid owing to the formation of basic antimony chloride. Similar products are obtained by the electrolysis of acid solutions of the bromide and iodide (Gore).

Uses. Antimony is employed for the preparation of tartar emetic, and of other pharmaceutical products which will be hereafter described. Its alloys are also largely used in the arts. When antimony is precipitated by zinc from a solution of the trichloride, the metal is obtained in a finely pulverulent state, as *antimony black;* this is employed for the purpose of imparting to the surface of gypsum figures and other objects the appearance of iron or steel.

[1] *Phil. Trans.* 1858, 185; 1859, 797; 1862, 323.

ANTIMONY ALLOYS.

529 Basil Valentine mentions that antimony is valuable for the preparation of medicines, and that it is likewise employed for other purposes, such as for the preparation of printer's type. He adds that under certain favourable conjunctions of the planets alloys are made of antimony, and from these seals and amulets are cast, which are said to possess special virtues. These same alloys can, according to Valentine, be cast in the same way to form both bells and mirrors.

English type-metal is an alloy of lead, antimony, and tin. A small percentage of copper is sometimes added, but found of little practical value.

The value of antimony in these alloys is that it imparts to them hardness, and gives them the property of expanding in the act of solidification so necessary in order to obtain an accurate cast of the letter. The tin gives toughness and coherence to the metal. The following are analyses of English type-metal;[1] No. I. is a specially tough metal:

	I.	II.	III.	IV.
Lead . .	50	55·0	61·3	69·2
Antimony.	25	22·7	18·8	19·5
Tin . . .	25	22·1	20·2	9·1
Copper .	—	—	—	1·7

German type-metal contains about 15 per cent. of antimony.

The best type-metal is obtained by fusing together two kilos. of tin and one kilo. of copper foil under finely divided charcoal. To this five kilos. of lead are added, and after it has been strongly heated two kilos. of antimony are introduced. To this is usually added 1 kilo. of ordinary type-metal, consisting of 25 kilos. of lead to 5 kilos. of antimony. The whole is cast at a low temperature in order to obtain as sharp a cast as possible.[2]

Britannia-metal and *Pewter.* This silver-white metal is largely used for the preparation of spoons, cups, and other articles. It

[1] Varrentrapp, *Dingl. Polyt. Journ.* clxxv. 38.
[2] *Ber. Entw. Chem. Ind.* i. 982.

consists mainly of tin and antimony, but frequently contains other metals, as is shown by the following analyses:

	Britannia Metal.		Plate Pewter.	Ashbury Metal.	Métal Argentin.
Tin . . .	85·7	81·9	89·3	77·8	85·5
Antimony .	10·4	16·2	7·1	19·4	14·5
Copper . .	1·0	—	1·8	—	—
Zinc . . .	2·9	1·9	—	2·8	—
Bismuth .	—	—	1·8	—	—

White- or *anti-friction-metal* is chiefly used for lining the brasses of various parts of locomotive engines, and for the solid bushes for the coupling-rods. Several alloys are used for this purpose, as is seen by the following analyses:

	I.	II.	III.
Copper	5·3	1·5	5·0
Antimony . . .	10·5	13·0	10·0
Tin	84·2	45·5	85·0
Lead	—	40·0	—
	100·0	100·0	100·0

No. I. is a metal used at the Crewe works; No. II. is one known as Babbit's metal; and No. III. one used by the German locomotive makers.

The alloy employed for the manufacture of ships' nails consists of 3 parts of tin, 2 of lead, and 1 of antimony.

Brass articles can be covered with a fine lustrous coating of antimony by dipping them into a hot solution of 1 part of tartar emetic, 1 of tartaric acid, and 3 of water, to which 3 or 4 parts of hydrochloric acid and as much powdered antimony has been added. The peculiar crystallographic relations of these alloys have been already referred to. (Vol. ii., Part i., page 9).

ANTIMONY AND HYDROGEN.

530 *Antimony Hydride*, or *Stibine*, SbH_3. This substance was first prepared in 1837 by Lewis Thompson,[1] and also, independently, by Pfaff[2] and other chemists. It is formed when nascent hydrogen is brought into contact with a soluble antimony compound, or when an alloy of potassium or sodium with antimony is decomposed by water, or an alloy of zinc and antimony by dilute hydrochloric or sulphuric acid. It is also formed when antimony oxide is added to an acid solution which is evolving hydrogen. All these methods, however, furnish a gas which is largely mixed with free hydrogen. According to F. Jones,[3] a relatively pure gas is obtained by allowing a concentrated solution of antimony in strong hydrochloric acid to drop slowly on to an excess of granulated or pulverized zinc. The gas thus obtained quickly undergoes partial decomposition, so that the interior of the evolution-flask becomes covered with a mirror-like coating of antimony, and the evolved gas contains at most 4 per cent. of antimony hydride. Stibine possesses a most disagreeable smell and taste. Water at 10° dissolves from 4 to 5 volumes, and fish die in a few hours in water thus saturated, but they recover if, when still alive, they are thrown into fresh water. Antimony hydride is easily inflammable, burning with a greyish flame and evolving white fumes of antimony oxide. When the gas is passed through a red-hot glass tube metallic antimony is deposited close to the heated spot in the form of a lustrous mirror, and if this be heated more strongly, small metallic globules are seen by the microscope to have been formed. Concentrated sulphuric acid decomposes the gas. Caustic alkali solution becomes deep brown when the gas is passed through it, and at last a black powder separates out. The brown solution absorbs oxygen rapidly, and especially if it be shaken with air. The brown powder thus obtained appears to possess the composition $Sb(OH)_3$. It rapidly decomposes on standing, becoming richer in antimony. When antimony hydride is passed through a solution of silver nitrate, black silver antimonide, $SbAg_3$, is deposited, mixed with metallic silver arising from the action of free

[1] *Phil. Mag.* [3], x. 353. [2] *Pogg. Ann.* xli. 339.
[3] *Chem. Soc. Journ.* 1876, i. 641.

hydrogen upon the silver salt. Sulphur decomposes the gas in sunlight or on heating to 100°, but not in the dark, and becomes itself covered with a film of the orange-red antimony sulphide (F. Jones):

$$2\ SbH_3 + 6S = Sb_2S_3 + 3H_2S.$$

Sulphuretted hydrogen acts in the sunlight in the same way:

$$2SbH_3 + 3H_2S = Sb_2S_3 + 6H_2.$$

ANTIMONY AND OXYGEN.

531 Considerable doubt formerly existed as to the number of the oxides formed by antimony. Thénard, in 1800, mentions several; whilst Proust, in 1804, admitted the existence of only two. The exact number was ascertained by Berzelius in 1812 to be as follows:

Antimony trioxide, Sb_2O_3.
Antimony tetroxide, Sb_2O_4.
Antimony pentoxide, Sb_2O_5.

All these are acid-forming oxides; the first acting also as a feebly basic oxide.

Antimony Trioxide, Sb_2O_3. This occurs as the mineral valentinite, with other ores of antimony, having been produced by the oxidation of these. It forms pearly-white rhombic crystals which are sometimes coloured yellow or red by the presence of iron and other metals, and have a specific gravity of 5·566. Another, though less frequent form of antimony trioxide, is senarmontite, which usually occurs together with other antimony ores, and crystallizes in regular octohedrons, having a specific gravity of 5·2 to 5·3. From this it appears that antimony trioxide is isodimorphous with arsenic trioxide. Both these crystalline forms can be artificially prepared. Thus when the metal or sulphide is heated in an inclined crucible a light white oxide is formed at a red-heat, and this, when more strongly heated, is deposited on the upper part of the crucible in glistening needles, sometimes mixed with octohedrons, and known as *flores antimonii*, or flowers of antimony. This latter form is also observed when the rhombic oxide is sublimed, and the octohedrons, when quickly heated, are converted into the rhombic

crystals.[1] Both forms are also obtained by crystallizing a hot saturated solution of the oxide or chloride in sodium carbonate (Mitscherlich). Antimony trioxide is prepared by diluting an acid solution with water, and washing the basic salts which are thrown down, first with hot water, then with soda solution, again with water, and finally converting the residue into oxide by ignition. Obtained in this way, the oxide is a pale buff-coloured crystalline powder, which can also be obtained by oxidizing the metal with very dilute nitric acid. It is scarcely soluble in water, and becomes yellow when ignited, but assumes the pale buff tint again on cooling.

At a dark red-heat it melts, and the mass obtained on cooling is crystalline. It is insoluble in sulphuric and nitric acids, but is easily soluble in hydrochloric and tartaric acids, and the caustic alkalis. The solution of antimony trioxide in tartaric acid or in cream of tartar yields *tartrate of antimony and potassium* or *tartar emetic*, $C_4H_4KSbO_7$. Heated in the air it absorbs oxygen. According to Bunsen the presence of higher oxides can be easily detected by the addition of potassium iodide to the hydrochloric acid solution when iodine is set free, as may be readily ascertained by shaking the liquid with a few drops of carbon disulphide.

The mineral valentinite was probably known to the ancients. Pliny states that two kinds of stibium exist: "*Duo ejus genera, mas et femina. Horridior est mas, scabriorque et minus ponderosus, minusque radians et arsenosior; femina contra nitet, friabilis, fissurisque, non globis, dehiscens.*" Perhaps, however, under the feminine variety he may have understood the preparation obtained by roasting the sulphide, for this process is mentioned by Dioscorides, and Glauber also refers to it. The operation is more fully described by Basil Valentine. He says: "From the common regulus of the spiessglas magnificently fine *flores* may be prepared both yellow, red, and white," by regulating the fire carefully. Valentine certainly knew that the mineral which we now call valentinite is an ore of antimony, for he distinguishes between the black- and the golden-spiessglas. The oxide obtained by roasting the metal reduced by iron was formerly called *nixferrum*, as it was believed that iron was necessary for its formation.

[1] Terreil, *Comptes Rendus*, lxii. 302.

ANTIMONIOUS ACID AND THE ANTIMONITES.

539 *Antimonious Acid*, $2HSbO_2 + 3H_2O$, is formed by adding copper sulphate to a solution of antimony sulphide in caustic potash until no further orange-coloured precipitate is thrown down, but a white precipitate is formed. After filtration the liquid, on addition of acetic acid, yields a precipitate having the above composition.[1]

Only the sodium antimonite has as yet been obtained in the crystalline condition.

Sodium Antimonite, $NaSbO_2 + 3H_2O$, separates out from a hot solution of the oxide in soda in glistening octohedrons which are difficultly soluble in water.

Hydrogen Sodium Antimonite, $NaH_2Sb_3O_6$, is obtained from very concentrated solutions in large crystals almost insoluble in water, which, like those of the former compound, appear to belong to the monoclinic system.[2]

ANTIMONIOUS AND HYPOANTIMONIC COMPOUNDS.

533 The corresponding haloid compounds will be decribed hereafter. The others are insoluble in water, being decomposed by it, especially when warm, with formation of basic salts, which, on long standing in contact with water, lose the whole of their acid, leaving a residue of trioxide.

Antimony Trisulphate, $Sb_2(SO_4)_3$, is obtained as a white mass by heating either the metal or the oxide with concentrated sulphuric acid. It crystallizes from a tolerably acid concentrated solution in long glistening silky needles,[3] and is decomposed by water into a soluble acid salt, and an insoluble basic salt. If antimony chloride be heated with fuming sulphuric acid, a basic salt, $Sb_2O(SO_4)_2$, is produced in small glistening crystals which in contact with alcohol are transformed into the salt $Sb_2O_2SO_4$, consisting of a white powder, which, when treated with boiling water, yields the salt $Sb_4O_5SO_4$.

[1] Schaffner, *Ann. Chem. Pharm.* li. 182.
[2] Terreil, *Ann. Chim. Phys.* [4], vii. 350.
[3] Schultz-Sellack, *Ber. Deutsch. Chem. Ges.* iv. 13.

Antimony Tetroxide or *Antimonious-Antimonic Oxide*, Sb_2O_4. By some chemists this substance is considered to be a compound of the trioxide and pentoxide of antimony. It is a white powder formed when either of the two other oxides is strongly heated in the air. When heated it becomes temporarily yellow, and dissolves only with difficulty in acids. Antimony-ash, obtained by roasting the sulphide in the air, is an impure tetroxide, and was formerly employed for the preparation of the antimony compounds. Impure tetroxide also occurs, as the mineral cervantite found together with other antimony ores in Tuscany. Antimony tetroxide forms salts with basic oxides which have been termed *hypoantimonates*.

Potassium Hypoantimonate, $K_2Sb_2O_5$, is obtained by fusing together the tetroxide and potash, and lixiviating the fused mass with cold water. It is a white mass which is soluble in hot water; on addition of hydrochloric acid to this solution the acid salt $K_2Sb_4O_9$ separates out.

Other insoluble hypoantimonates can be obtained by double decomposition with the corresponding salts. Some of these occur as minerals. Thus romeite, $CaSb_2O_5$, crystallizes in quadratic pyramids, and is found at St. Marcel, in Piedmont; and ammiolite, which occurs as a powder coloured red by the presence of cinnabar, found at Chili, is probably a copper hypoantimonate, $CuSb_2O_5$.

ANTIMONY PENTOXIDE AND ANTIMONIC ACIDS.

534 *Antimony Pentoxide*, Sb_2O_5, is obtained by rapidly evaporating the powdered metal or its lower oxides with nitric acid, and gently heating the residue. It is a light yellow powder, having a specific gravity of 5·6, practically insoluble in water, and turning blue litmus-paper red. Nitric acid does not dissolve it, whilst concentrated hydrochloric acid only attacks it slowly, but at last dissolves it completely; it volatilizes completely when heated with sal-ammoniac. It likewise forms two hydroxides, antimonic and metantimonic acids, which give rise to two series of salts.

Antimonic Acid, $HSbO_3 + 2H_2O$, is obtained by decomposing one of its salts with sulphuric or nitric acid. It was formerly known under the name of *materia perlata*, and was employed as

a medicine. It is an impalpable white powder, which is slightly soluble in water, and which becomes anhydrous on gentle ignition. Antimonic acid dissolves readily in potash, but is insoluble in cold ammonia.

Metantimonic Acid, $H_4Sb_2O_7$, is formed by the decomposition of the pentachloride by water. The air-dried precipitate possesses the formula $H_4Sb_2O_7 + 2H_2O$,[1] and has the same composition as volgerite, a mineral which occurs in the province of Constantine, in Algeria. When dried at 100° it becomes anhydrous, and it dissolves rather more readily in water than antimonic acid, and also is soluble in cold ammonia. By heating to 200°, or when kept under water, it is converted into antimonic acid.

THE ANTIMONATES AND METANTIMONATES.

535 Since the time of Berzelius, the antimonates have been chiefly investigated by Fremy[2] and Heffter,[3] and the metantimonates have been prepared by Fremy.

Potassium Antimonate, $KSbO_3$, is obtained by deflagrating one part of metallic antimony with four parts of saltpetre and lixiviating with warm water. A white powder is thus obtained, which when boiled for some time with water dissolves to a considerable extent. On concentrating the solution to a certain point, a crystalline mass separates, but if the liquid be further evaporated, a gum-like mass, $2KSbO_3 + 5H_2O$, is obtained, which dissolves readily in warm water. When a current of carbon dioxide is passed through a solution of the normal salt, the acid salt, $2KSbO_3 + 2HSbO_3 + 5H_2O$, is formed as a shining white powder; and if the normal salt be boiled for some time with water, a residue having the composition $4KSbO_3 + 2HSbO_3 + 9H_2O$ is obtained. This salt was probably known to Basil Valentine, and was much employed by quack doctors and known as *antimonium diaphoreticum ablutum*. The substance obtained by deflagrating the sulphide with saltpetre was employed at the end of the 17th century under the name *antimonium diaphoreticum non ablutum*, and Libavius and others treated this residue with acids in order to obtain their diaphoreticum, which, therefore, consisted chiefly of antimonic acid.

[1] Daubrawa, *Liebig's Ann.* clxxxvi. 110.
[2] *Ann. Chim. Phys.* [3], xii. 499, and xxiii. 407.
[3] *Pogg. Ann.* lxxxvi. 418.

Sodium Antimonate, $2NaSbO_3 + 7H_2O$, is obtained when the metal or sulphide is deflagrated with Chili saltpetre and the mass washed out with water. At 200° it loses two molecules of water, but it does not become anhydrous until it attains a red-heat.

Ammonium Antimonate, NH_4SbO_3, is formed by dissolving the acid in warm ammonia. It separates out on cooling as a crystalline powder, which is insoluble in water, and readily gives off ammonia.

The antimonates of metals of the other groups are either difficultly soluble or insoluble in water. They may be obtained by double decomposition as crystalline precipitates, which are decomposed by weak acids with formation of acid salts, whilst stronger acids, on the other hand, liberate antimonic acid. Almost all the antimonates dissolve in strong hydrochloric acid.

Normal Lead Antimonate, $Pb(SbO_3)_2$, is a white curdy precipitate, insoluble in water. The *basic salt,* $Pb_3(SbO_3)_2(OH)_4 + 2H_2O$, occurs as bleinierite, at Nertschinsk, in Siberia, and Endellion, in Cornwall, in reniform or spheroidal masses, which possess a resinous appearance and a white grey, brown, or yellowish colour. Another basic salt which is used in oil painting, under the name of Naples Yellow, is obtained by heating a mixture of one part of tartar emetic, two parts of lead nitrate, and four parts of common salt, for two hours to the fusing-point of chloride of sodium, and then lixiviating with water.

Normal Potassium Metantimonate, $K_4Sb_2O_7$, is best obtained by fusing the ordinary gelatinous antimonate with three times its weight of potash, dissolving the fused mass in water, and evaporating. It is thus deposited in deliquescent warty crystals, which are decomposed by water into free alkali and an acid salt, $H_2K_2Sb_2O_7 + 6H_2O$, forming a crystalline powder difficultly soluble in cold water, but more readily in water at a temperature of from 40° to 50°. In solution it easily decomposes into gelatinous antimonate, and when heated to 200° it is converted into the anhydrous salt, and passes at 300° into ordinary potassium antimonate.

Sodium Metantimonate. The normal salt has not been investigated. The *acid sodium metantimonate,* remarkable as being the only insoluble salt of sodium, has the composition $H_2Na_2Sb_2O_7 + 6H_2O$, and is quite insoluble in cold, and dissolves only sparingly in hot water. It is obtained as a crystalline precipitate, which is

gradually deposited when a solution of the potassium metantimonate is added to a sodium salt. This compound is employed as a reagent for the detection of sodium. Even when a solution contains only 0·1 per cent. of sodium salt, a crystalline powder separates out after standing for twelve hours. Addition of alcohol facilitates the precipitation ; free alkalis, on the other hand, retard its formation. The salts of lithium, ammonium, and the metals of the alkaline earths, give precipitates with potassium metantimonate, and hence these substances must be removed from solution before the above test for sodium can be applied.

Normal Ammonium Metantimonate, $(NH_4)_4Sb_2O_7$, is only known in solution, and is obtained by treating the acid with ammonia. When alcohol is added to this solution, a crystalline precipitate of $H_2(NH_4)_2Sb_2O_7 + 5H_2O$ is thrown down, and this readily undergoes change into the ordinary antimonate.

The ordinary antimonates stand in the same relation to the meta-salts as the metaphosphates stand to the pyrophosphates, and, therefore, by good rights they should thus be named. The adoption of this nomenclature would, however, introduce confusion, as the above names are now in common use.

ANTIMONY AND CHLORINE.

536 *Antimony Trichloride,* $SbCl_3$. Basil Valentine says: "Take of fine white, well-sublimed corrosive sublimate, and of good spiessglas the same quantity. Rub these up together and distil them. The oil which comes over is at first white, and congeals like ice or clots of butter." This preparation was termed *butyrum antimonii,* and was supposed to contain quicksilver until Glauber, in 1648, showed that this was not the case, inasmuch as it could be prepared by distilling spiessglas with oil of vitriol and common salt or hydrochloric acid. Several other methods of preparation may be mentioned, as, for example, by heating sulphate of antimony with sodium chloride, as well as by heating an excess of metallic antimony, or its sulphide, in a current of dry chlorine.

Antimony trichloride is a crystalline mass, melting at 72° and boiling at 223°. Its colourless vapour has a specific gravity of 8·1. On exposure to moist air the solid deliquesces to a clear liquid, and this, on evaporation over sulphuric acid, yields crystals of the anhydrous chloride. A solution of the chloride

is best obtained by boiling the sulphide with strong hydrochloric acid. When this is distilled in a retort, water comes over first, next the excess of hydrochloric acid, and lastly, the anhydrous chloride. The concentrated solution, which has a specific gravity of 1·35, is known as *liquid butter of antimony*, and is employed for giving a brown surface to iron and steel wares, such, for instance, as gun-barrels (brown Bess); it is also sometimes used for pharmaceutical purposes. The anhydrous chloride yields with dry ammonia the brittle white compound, $SbCl_3.NH_3$, which, on heating, gives off ammonia. It also forms soluble crystalline double salts with a variety of metallic chlorides.

537 *Powder of Algaroth.* If the acid solution of the chloride be diluted with water, a white precipitate of the basic chloride is thrown down. This precipitate was known to Basil Valentine; and Paracelsus, who employed it as a medicine, states in his *Archidoxa*, that in order to prepare it, corrosive sublimate is to be distilled with antimony, and the product coagulated with water, when the *mercurius vitæ* is obtained. Towards the end of the sixteenth century it was much employed, especially by the Veronese physician, Algarotus, and termed by him *pulvis angelicus*, although it has been generally known as *powder of Algaroth*. The presence of tartaric or free hydrochloric acid prevents the precipitation of this substance. Its composition varies according to the method of its preparation. If ten parts of solid trichloride are mixed with seventeen parts of water, and allowed to stand until the precipitate has become crystalline, the compound SbOCl is deposited in small rhombohedrons. These may be washed with ether in order to remove the excess of the chloride. The same compound is obtained by heating equal molecules of the trichloride and absolute alcohol in sealed tubes to 140°. If one part of the trichloride be mixed with three parts of water, and the precipitate filtered off quickly and mixed with ether, the same body is obtained in the form of an amorphous powder. When this substance is heated the trichloride is given off, and the oxychloride, $Sb_4O_5Cl_2$, remains behind. The last-named compound is formed as an amorphous precipitate when the chloride is mixed with from five to fifty parts of water; on standing, it gradually becomes crystalline, forming silky prisms. If three times its bulk of hot water be added to the trichloride, and the liquid allowed to stand at 60° for some hours, crystals are obtained resembling

soda-crystals, which also possess the composition $Sb_4O_5Cl_2$.[1] When larger quantities of water are employed still more basic chlorides are formed, and if these are boiled repeatedly with water, they are converted into the trioxide, this reaction taking place more quickly in the presence of sodium carbonate. If antimony oxide be dissolved in boiling antimony trichloride, a pearl-grey crystalline mass is obtained on cooling, having the composition $SbOCl + 7SbCl_3$, and this compound yields the substance $2SbOCl + Sb_2O_3$ on treatment with absolute alcohol. Antimony trisulphide in a similar way forms the compound $SbSCl + 7SbCl_3$, which is deliquescent, and is converted by absolute alcohol into the reddish-yellow amorphous compound $2SbSCl + 3Sb_2S_3$.

538 *Antimony Pentachloride*, $SbCl_5$, was discovered by H. Rose in 1835, and is prepared by the direct union of antimony and chlorine, which takes place with evolution of light and heat. It is also readily formed by saturating the fused trichloride with chlorine gas. Antimony pentachloride is a colourless, fuming, disagreeably-smelling liquid, which solidifies in a freezing mixture forming crystals melting at $-6°$. It is readily volatile, partially decomposing on distillation into chlorine and trichloride, and is highly hygroscopic, dissolving to a clear liquid in a small quantity of water, from which, when placed over sulphuric acid, crystals of $SbCl_5 + 4H_2O$ deposit. An excess of water decomposes it with formation of the white oxychloride, SbO_2Cl, which is converted by hot water into antimonic acid. When mixed at once with a large excess of water the liquid remains clear. Tartaric acid, and a large excess of hydrochloric acid, prevent the precipitation by water. As it easily loses chlorine, antimony pentachloride is employed in organic chemistry for the chlorination of many bodies. With hydrocyanic acid it forms the white crystalline compound $SbCl_5 + 3HCN$, which volatilizes under 100° with partial decomposition. It also forms compounds with various chlorides, such as $SbCl_5 + SCl_4$, $SbCl_5 + PCl_5$, $SbCl_5 + POCl_3$; these are solid bodies.

Antimony Oxytrichloride, $SbOCl_3$, is obtained when the pentachloride, well cooled with ice, is mixed drop by drop with the requisite quantity of water. It is a yellow crystalline mass, which deliquesces on exposure to moist air.[2] When three molecules of antimony pentachloride are heated with one molecule of

[1] Sabanajew, *Zeitsch. Chem.* 1871, 204.
[2] Daubrawa, *Liebig's Ann.* clxxxvi. 110.

pentoxide to 140°, two oxychlorides are obtained, viz., Sb_3OCl_{13} and $Sb_3O_4Cl_7$, which, as they melt at different temperatures, can be separated one from the other. The first is a white crystalline extremely deliquescent mass, which melts at 85°, whilst the other forms yellowish crystals, which melt at 97°·5.[1]

ANTIMONY AND BROMINE.

539 *Antimony Tribromide*, $SbBr_3$. Powdered antimony combines directly with bromine with evolution of light and heat. The tribromide sublimes in colourless deliquescent needles, which melt at 95°, and boil at 275°: water decomposes it with formation of a basic bromide. Another method of preparation consists in heating an excess of powdered antimony with a solution of bromine in carbon disulphide; the tribromide thus obtained on evaporation crystallizes in octohedrons.

A pentabromide does not exist.

ANTIMONY AND IODINE.

Antimony Triiodide, SbI_3. These elements combine together directly with evolution of so much heat that if large quantities are employed explosions may ensue. It is a brownish-red crystalline mass, yielding a cinnabar-red powder, and crystallizing in six-sided tablets from solution in hot carbon disulphide. On heating it melts to a garnet-red liquid, and forms a violet-red vapour, which at a higher temperature becomes scarlet. It sublimes easily at a temperature slightly above its melting-point, and is decomposed by water, with formation of a yellow oxy-iodide, which forms crystalline double salts with the various iodides.

The existence of a penta-iodide has not been satisfactorily established.

ANTIMONY AND FLUORINE.

Antimony Trifluoride, SbF_3, is obtained as a dense snow-white mass, by distilling antimony with mercury fluoride. If a solution of the oxide in an excess of hydrofluoric acid be evaporated, the fluoride is also obtained, in rhombic pyramids. It is deliquescent, and is not decomposed by water; but if the solution be

[1] W. Carleton-Williams, *Journ. Chem. Soc.* 1872, 122.

evaporated without an excess of hydrofluoric acid a basic fluoride is formed. Antimony trifluoride forms fine crystalline double salts with the fluorides of the alkali-metals containing one molecule of the trifluoride to one, two, or three molecules of the alkaline fluoride.

Antimony Pentafluoride, SbF_5, is obtained by dissolving antimonic acid in hydrofluoric acid. On evaporation a gummy mass remains which is decomposed on heating. It forms with the fluorides of the alkali-metals difficultly crystallizable double salts.[1]

ANTIMONY AND SULPHUR.

540 *Antimony Trisulphide*, Sb_2S_3, occurs crystallized as stibnite in the older stratified rocks. This is the most important ore of antimony, and it is found in considerable quantity, occurring in Cornwall, Hungary, Transylvania, in the Banat, in the Harz, in Westphalia, in the Black Forest, in Bohemia, in the Auvergne, in Estramadura, Algiers, Corsica, Siberia, Nevada, New Brunswick, and especially, in large quantities, in Borneo. It crystallizes in prisms, but is usually found in columnar or striated masses, which soil the fingers like graphite. It is easily pulverisable, and readily fusible, and has a specific gravity of 4·62. The crude sulphide occurring in commerce is obtained by melting the ore in the manner already described, and is sold in rounded masses having the form of the vessel in which the molten sulphide solidifies. It has a metallic lustre, steel-grey streak, and crystalline fracture. From early times this substance has been long used in the East under the name of Kohl. It is employed in medicine. The alchemists occupied themselves much with the properties of this body, as it was used for the purification of gold, and was termed *judex ultimus*, or *lupus metallorum*. Antimony trisulphide also exists in the amorphous state, and in this form was known to Basil Valentine, being prepared by a method to which but little or no attention was afterwards paid. He states that crude spiessglas may be sublimed with formation of a red body when it is mixed with *sal ammoniacum*. In this way antimony chloride and ammonium sulphide are formed, which again react on cooling, producing the original compounds, the antimony sulphide sepa-

[1] Marignac, *Ann. Chem. Pharm.* cxlv. 239.

rating out as a red powder. Glauber, and also Lemery, speak of the solution and the subsequent precipitation of the spiessglas with caustic alkalis; but it was not until 1714 that attention was directed to the red sulphide of antimony. In the above year a Carthusian monk whose life had been despaired of by the Paris faculty, was saved by a monk of the name of Simon administering to him a medicine which was first prepared by a German apothecary, a disciple of Glauber, and which was bought by the Parisian apothecary De la Ligérie. This was soon known as the "poudre des chartreux" or Carthusian powder. Simon, however, gave to it the name of *Alkermes mineral*, and such was the reputation which this medicine enjoyed that the French Government bought the receipt for its preparation in 1720 from De la Ligérie. The process consisted in boiling the spiessglas with potashes and allowing the clear solution to cool when the kermes was deposited as a red powder. In 1728 Stabel found that when caustic potash was employed, a red powder was also obtained, which Mender in 1738 showed to be the pure kermes, and C. J. Geoffroy in 1735 proved that the same preparation was obtained when spiessglas is fused with carbonates of the alkali-metals, and the liver of antimony thus obtained boiled with water. This body was believed to be a compound of antimony, sulphur, and alkali, though chemists such as Baumé denied that it contained any alkali, and assumed that in spiessglas regulus of antimony was combined with sulphur, whilst in mineral kermes calx of antimony was combined with sulphur. Many other views were held concerning the composition of this compound until Rose in 1825, and Fuchs in 1833, showed that mineral kermes is nothing more than amorphous antimony sulphide.

Various methods may be employed for the preparation of mineral kermes, which for fifty years was highly prized as a medicine, and even now is sometimes employed. All these processes yield a preparation containing, as impurity, varying quantities of antimony oxide, both free and combined with the alkalis. Hence the preparation of the kermes should be carried on exactly according to the prescription of the pharmacopœia.

In order to prepare the amorphous sulphide free from oxide, the crystalline compound is boiled with caustic potash in absence of air, the liquid filtered and the hot diluted solution precipitated with sulphuric acid. The precipitate is then washed with

very dilute acid and afterwards with cold water; and to remove any oxide which may be present it is heated with a solution of tartaric acid. Thus obtained the precipitate becomes anhydrous when dried at 100° and forms a reddish-brown light powder which readily soils the fingers. This is more soluble in hydrochloric acid, in the fixed alkalis, and their carbonates than the crystalline compound into which it is converted on fusion. It may also be obtained by pouring fused stibnite into an excess of cold water. It then forms an amorphous lead-grey mass which appears of a hyacinth-red colour when seen in thin films, has a specific gravity of 4·15, and when triturated is converted into a dark reddish-brown powder.

If sulphuretted hydrogen be passed into an acid solution of the trichloride or into an acidified solution of tartar-emetic, an orange-red precipitate of amorphous hydrated sulphide is obtained which on drying at 200° becomes anhydrous and black. On heating in a current of hydrogen the trisulphide is reduced to metal, but it may be sublimed without decomposition in an atmosphere of nitrogen. Crystalline antimony sulphide is used not only for the preparation of the other antimony compounds, but also in pyrotechny, and for the preparation, especially in Sweden, of the heads of lucifer matches, as well as for the composition used for firing breechloading fire-arms. The amorphous sulphide is largely used as a means for vulcanising caoutchouc, to which it also imparts a reddish-brown colour.

The Thioantimonites or *Livers of Antimony* are formed by the combination of the trisulphide with basic sulphides. Those of the alkali metals are prepared by fusing the constituents together. They are brown or black, and when they contain a large quantity of basic sulphide they are easily soluble in water, but when the quantity of antimony increases, these livers of antimony become more difficultly soluble, and at last insoluble in water. The same compounds are formed when the trisulphide is dissolved in an aqueous solution of a sulphide, mixed with antimonite, or when the trisulphide is fused with the alkali or alkaline carbonate:

$$2Sb_2S_3 + 4KOH = 3KSbS_2 + KSbO_2 + 2H_2O.$$

Acids precipitate the amorphous trisulphide from these solutions, which also absorb oxygen rapidly from the air. Many of the thioantimonites occur as minerals, and the composition of these has been already given.

541 *Antimony Pentasulphide,* Sb_2S_5. This compound does not occur in the native state. Basil Valentine mentions that when spiessglas is boiled with strong caustic ley, and acetic acid added to the liquor a red body is precipitated, and Quercetanus in 1603 mentions in his pharmacopœia a preparation from spiessglas and liver of sulphur by means of acids terming it *sulphur antimonii auratum.* In 1654 Glauber mentions in the "pharmacopœia spagyrica" the preparation obtained by precipitating the slag obtained in the preparation of regulus of antimony by means of acetic acid, and recommends this product as *panacea antimonialis* or *sulphur purgans universale.* This preparation, which was known as golden sulphuret of antimony, soon became a favourite medicine. It was obtained from the more or less oxidized solution of liver of antimony, containing a thioantimonate. If this be fractionally precipitated by hydrochloric acid, a brown kermes is first thrown down and afterwards a golden coloured sulphide, which has therefore been termed *sulphur auratum tertiæ præcipitatonis.* In later times stibnite was boiled with alkali with addition of sulphur and the solution precipitated with acid. At the present day pure thioantimonate is first prepared, and for this purpose the well-crystallized sodium salt is employed; this is dissolved in from 10 to 60 parts of water and a cold mixture of 3·3 parts of sulphuric acid and 100 parts of water is gradually added; the precipitate is well washed with distilled water and dried at a moderate temperature in the dark.

Antimony pentasulphide is a fine yellowish-red powder easily soluble in aqueous alkalis and their sulphides, and also, in absence of air, in warm ammonia. It likewise dissolves in the carbonates of the alkali metals, but not in carbonate of ammonia. Heated in absence of air it decomposes into the trisulphide and sulphur, and when boiled with hydrochloric acid sulphur separates out, sulphuretted hydrogen is evolved, and the trichloride is found in solution.

Sodium Thioantimonate, $Na_3SbS_4 + 9H_2O$. This is termed, from the discoverer, *Schlippe's salt,* and is obtained by dissolving the trisulphide, sulphur, and caustic soda or a mixture of soda ash and lime, in the requisite quantity of water; or by fusing together 16 parts of anhydrous sodium sulphate, 13 parts of stibnite, and 5 parts of carbon, dissolving, and boiling the solution with 2·5 parts of sulphur. It crystallizes in large colourless or yellow regular tetrahedrons which have an alkaline reaction

and a saline cooling bitter metallic taste resembling that of liver of sulphur. It dissolves at 15° in 2·9 parts of water and is precipitated from aqueous solution by alcohol. The hydrated crystals on exposure to moist air soon become covered with a kermes-coloured coating, and heated in absence of air water is given off and the anhydrous salt formed. This fuses at a dark red-heat yielding on solidification a brown soluble mass.

Potassium Thioantimonate, $K_3SbS_4 + 9H_2O$, is prepared in a similar way to the sodium salt and forms deliquescent crystals.

Barium Thioantimonate, $Ba_3(SbS_4)_2 + 6H_2O$, is prepared by dissolving the freshly precipitated golden sulphide of antimony in barium monosulphide and precipitating by alkali. In this way groups of stellated needles are obtained.

The *calcium* salt is prepared in a similar way and is thrown down as an oily liquid on addition of alcohol.

The thioantimonates of the other groups are almost entirely insoluble in water and are obtained by double decomposition between their soluble salts and sodium thioantimonate. They are yellow, red, brown, or black precipitates.

542 *Antimony Oxysulphide*, SbS_2O, is found, together with stibnite, as kermesite or antimony blende in needle-shaped crystals or thin six-sided prisms which have a cherry-red colour and an almost metallic lustre. The same compound is obtained as a reddish-brown powder by adding antimony trisulphide to fused antimony iodide, and treating the mass with dilute hydrochloric acid when a dark reddish-brown lustrous powder of antimony thioiodide, SbSI, remains behind, and this, when boiled with water and oxide of zinc, is converted into the oxysulphide.

A compound probably having the same composition is known as *antimony cinnabar*, and is obtained by warming a solution of the trichloride with sodium thiosulphate. This substance is used in oil-painting as well as in water-colour painting and as a distemper.

Both the following preparations, which were first described by Basil Valentine and were formerly made use of, also contain antimony oxysulphide.

Glass of Antimony or *vitrum antimonii* is obtained by fusing oxidized stibnite with a small quantity of the sulphide. It forms a transparent dark ruby-red mass, formerly largely employed for obtaining the other antimony compounds, but now, however, only used for imparting a yellow tint to glass and porcelain.

Antimonial Saffron or *crocus antimonii.* If stibnite be deflagrated with a quantity of saltpetre insufficient for complete oxidation, a brownish-yellow powder is obtained on lixiviation which when heated melts to a yellow glass.

ANTIMONY AND SELENIUM.

543 *Antimony Triselenide*, Sb_2Se_3, is formed when the two elements are fused together, a metallic lead-grey crystalline mass being produced. When selenium hydride is passed into a solution of tartar emetic, the same compound is precipitated as a black powder.

Antimony Pentaselenide, Sb_2Se_5, is precipitated as a brown powder by adding dilute sulphuric acid to a solution of sodium seleno-antimonate.

Sodium Seleno-antimonate, $Na_3SbSe_4 + 9H_2O$, is isomorphous with the corresponding, thio-antimonate, and is obtained by fusing together 4 parts of sodium carbonate, 6 parts of antimony triselenide, 3 parts of selenium, and 1 of charcoal. The fused mass is boiled out with water in absence of air and the filtrate covered with a layer of strong alcohol. The salt separates out after some time in orange-red transparent tetrahedrons which are soluble in two parts of cold water and become red-coloured on exposure to air, with separation of selenium. When a solution of Schlippe's salt is boiled with selenium, filtered, and the solution concentrated in absence of air, yellow tetrahedrons of $Na_3SbSeS_3 + 9H_2O$ are deposited.

Antimony and *tellurium* when fused together yield, according to the proportions employed, either an iron-grey metallic lustrous mass, or a tin-white *antimony tritelluride.*

If *phosphorus* be added to fused antimony, a tin-white phosphide of antimony is obtained which when heated in the air burns with a greyish flame.

Antimony combines directly with *arsenic.* The compound Sb_2As_3 occurs as allemontite in reniform or amorphous masses having a metallic lustre.

Medicinal Uses of Antimony.

544 As we have seen, various antimony preparations are used as important medicines. Basil Valentine was the first to employ these for inward use, and his example was followed by Paracelsus and other iatro-chemists, many of whom worked diligently on antimony and its compounds. The disciples of the old Galenic school were violently opposed to the introduction of the antimony compounds into medicine, and they succeeded in inducing the Paris Parliament in 1566 to prohibit the use of antimony and its compounds by all physicians on pain of having their licenses withdrawn. In 1603 the medical faculty of Paris took a similar step, and this decree was not withdrawn until the year 1666.

Metallic antimony itself was at one time employed for the preparation of goblets in which wine was allowed to stand over-night in order that it might be used as an emetic; but this practice fell into disuse even during Boyle's time. Pills made of metallic antimony were employed at a later period: these were termed everlasting pills, because they, like the goblets, were believed only to act by contact and not to lose their weight. This error was first combated by Lemery and Vigani, a Veronese quack doctor who lived in England, and they showed that both antimony and fused stibnite became acted upon when placed in contact with wine.

Whilst formerly a large number of antimony compounds were employed in medicine, the only ones which are used at the present day are tartar emetic or potassium antimonyl tartrate, $C_4H_4K(SbO)O_6$; and the trisulphide or *antimonium sulphuratum*. The first compound is given in doses of $\frac{1}{16}$ to $\frac{1}{8}$ of a grain as a diaphoretic, and from 1 to 2 grains as an emetic. The dose of the second is from 1 to 5 grains.

In larger doses it produces, like white arsenic, violent irritation in the intestines, vomiting and purging. When one large dose only is administered, the case proceeds rapidly to recovery or death, the former generally, if the case is placed early under proper treatment, and in this respect acute antimonial is distinguished from acute arsenical poisoning.

In cases of chronic antimonial poisoning the principal symptoms are great nausea, vomiting of mucous and bilious liquids, great depression, purging, and finally death from complete ex-

haustion. Several cases have occurred in this country to show that tartar emetic has been thus criminally and fatally used (Taylor).

Detection and Estimation of Antimony.

545 When a small quantity of an antimony compound is heated in the upper reduction zone of a Bunsen burner on a thread of asbestos the flame becomes of a bluish tinge, and when a small porcelain basin filled with cold water is held above it a brownish-black deposit of metallic antimony is found upon the basin, and this is but slightly attacked by cold nitric acid, and is insoluble in sodium hypochlorite. Arsenic gives a very similar reaction (see Vol. I. p. 539), but this may be distinguished from antimony by the fact that during the reduction a garlic-like smell of arsenic is noticed, and the metallic film is readily soluble in sodium hypochlorite. If an antimony compound be heated on a carbonized match, a brittle metallic bead is obtained, whilst arsenic is completely volatilised. Most of the antimony compounds are insoluble in water, but dissolve in hydrochloric acid. Those which do not thus dissolve may be obtained in solution by fusion with carbonate of potash and saltpetre, and subsequent solution in hydrochloric acid. Sulphuretted hydrogen produces in acid solutions a very characteristic orange-red coloured precipitate of antimony trisulphide. If other metals precipitable by sulphuretted hydrogen be present, the mixed sulphides, after washing, are treated with ammonium sulphide, filtered, and the filtrate acidified with hydrochloric acid. This precipitate may contain, together with antimony, the sulphides of tin and arsenic. The latter metal is removed by digestion with freshly-prepared solution of carbonate of ammonia, and washing the residue with water. This is then brought into solution by heating with hydrochloric acid, and the liquid is placed in a platinum dish containing a few pieces of zinc, when the antimony is deposited upon the platinum as a black adherent coating, whilst the tin separates out on the zinc in the form of a dull grey powder. This spongy tin readily dissolves in hot hydrochloric acid, whilst the deposit of antimony does not do so, but is readily soluble in nitric acid. If the nitric acid solution be evaporated with some hydrochloric acid, diluted with water, and treated with sulphuretted hydrogen, the characteristic precipitate of antimony sulphide is obtained.

Arsenic, antimony, and tin may also be separated by bringing their hydrochloric acid solution into a Marsh's apparatus, and passing the gas which is evolved through a solution containing silver nitrate when a precipitate of silver antimonide, $SbAg_3$, and of metallic silver is thrown down, the whole of the arsenic remaining in solution, whilst the tin is found in the metallic state precipitated uponthe zinc in the evolution flask.

Antimony trichloride gives a spark-spectrum containing the following lines mentioned in order of their relative brightness (Lecoq de Boisbaudran):

$$\alpha\ 6002 \qquad \beta\ 5568 \qquad \gamma\ 6127 \qquad \delta\ 6077.$$

Antimony is usually estimated either as the sulphide or the tetroxide. In the first case it is obtained as a hydrated precipitate, which may also contain sulphur and pentasulphide. It is necessary, therefore, to dry this at 100°, to weigh it, and to bring a known fraction into a porcelain boat contained in a glass tube. Through the tube dry carbon dioxide is passed, and the sulphide heated, the pure anhydrous trisulphide remaining behind. Bunsen, however, prefers to determine antimony as the pentasulphide, according to a method which will be described hereafter, by means of which it can be completely separated from any arsenic with which the antimony may be associated.

The *quantitative* separation of antimony from other metals, with the exception of arsenic and tin, does not exhibit any difficulty. Should these three elements be present together their sulphides must be first converted into oxide by treatment with nitric acid, and these fused for some time with eight times their weight of caustic soda. The cooled mass is next allowed to soften in hot water until the sodium metantimonate has separated out as a white powder, and then one volume of alcohol of specific gravity 0·83 is added for every three volumes of the liquid. After standing for some time the liquid is filtered and the precipitate well washed with dilute alcohol, to which at last some caustic soda is added. The filtrate contains the stannate and arsenate, whilst the whole of the antimony is contained in the residue, and this is converted in the usual way into the sulphide (H. Rose).

The separation of antimony from arsenic which hitherto was difficult and unsatisfactory, has lately been simplified and rendered easy by Bunsen. The moist and well washed mixture of sulphides obtained by precipitation with sulphuretted hydrogen

is dissolved on the filter by an excess of caustic potash, and the diluted solution heated with chlorine until all the free alkali has been combined. The excess of chlorine is then got rid of by repeated evaporation with hydrochloric acid, the solution diluted, and this heated with a freshly prepared solution of sulphuretted hydrogen until all the antimony is precipitated. A rapid current of air is then passed through the liquid in order to expel the excess of sulphuretted hydrogen, and the precipitate washed first with water, then with alcohol, and at last repeatedly with carbon disulphide, in order to remove free sulphur. After drying at 110° pure pentasulphide of antimony remains, and this is afterwards weighed. The arsenic in the filtrate may be estimated by subsequent continued treatment with sulphuretted hydrogen when the pentasulphide is precipitated, and treated as above described.

546 *Atomic Weight.* The number 129 found by Berzelius was long assumed to be correct, until Schneider's[1] experiments proved that 120 was nearer the truth. At a later date Dexter[2] again determined the atomic weight by converting the metal into the tetroxide. In ten experiments in which from 1·5 to 3·3 grams. were taken, he found that 100 parts of the oxide contain from 79·286 to 79·253, or in mean 79·266 parts of metallic antimony. Hence the atomic weight 122 is obtained, and the subsequent experiments of Dumas[3] and of Kessler[4] confirm this result. General considerations also lead to the conclusion that this number is the most probable, for, as has already been mentioned under titanium, the difference between the atomic weights of analogous elements remains nearly the same. In this case we have:

Sn = 64·9	As = 74·9	Br = 79·75
Cd = 111·6	Sb = 122·0	I = 126·53

On the other hand, it must be mentioned that a very accurate series of experiments has recently led J. P. Cooke[5] to the conclusion that 120 is the true atomic weight of antimony when that of sulphur is 32.

[1] *Pogg. Ann.* xcviii. 293.
[2] *Pogg. Ann.* c. 563.
[3] *Pogg. Ann.* cxiii. 145.
[4] *Ann. Chim. Phys.* [3], lv. 129.
[5] *Sill. Amer. Journ.* [3], xv. 41 and 107.

BISMUTH, Bi = 210.

547 The word *marcasite* by which, up to recent times the metal bismuth was often designated, is found in the authors of the thirteenth century. Hence it has been supposed that this metal was known at that time. This is, however, not the case, for the name marcasite had in those days, and even at a much later period, a very indefinite meaning, being given to any ore which had a metallic appearance, and especially to those ores which are now classed as pyrites.

Metallic bismuth was first described by Basil Valentine in his Last Testament: "Antimonium must be placed between tin and lead, as bismuth or magnesia is placed under and between tin and iron," and he also states that "bismuth or marcasite is a bastard *jovis*." In the following century bismuth was classed by Paracelsus amongst the semi-metals. On the other hand, Agricola mentions *bisemutum* or *plumbum cinereum*, as a true metal which is usually added to tin in order to make it work better. Notwithstanding this clear statement, it was subsequently confounded by Libavius with antimony, and by Lemery with zinc. Pott, in 1739, was the first to make us acquainted with the special properties of bismuth, and its reactions were exactly studied by Bergman.

Bismuth is a comparatively rare metal. It is found chiefly in the native condition, but also as the oxide or bismuth ochre, Bi_2O_3; less frequently it occurs as bismuthite, Bi_2S_3, whilst it is found still more sparingly in the following minerals: telluric bismuth, or tetradymite, Bi_2Te_3; emplectite, $Cu_2Bi_2S_4$; bismutite, $3(BiO)_2CO_3 + 2Bi(OH)_3 + 3H_2O$; aikinite, $(PbCu_2)_3Bi_2S_6$; pucherite, $BiVO_4$; eulytine or bismuth silicate, $Bi_4(SiO_4)_3$, &c.

Professor Winckler of Freiberg[1] has recently published an interesting paper on the smelting of bismuth and its uses in the arts, from which we make the following extracts.

The chief sources of bismuth are the Saxon smalt works, in Oberschlema and in Pfannenstiel, where the bismuth occurs at Schneeberg. Formerly bismuth was obtained by simply heating the ore in sloping iron tubes. In this way merely that portion of the metal present in the native state was obtained, and this only in a very incomplete manner. The residue was employed

[1] *Ber. Entw. Chem. Ind.* i. 953.

in the manufacture of smalt, and the bismuth again extracted from the cobalt-speiss. At the present day all bismuth ores are roasted and afterwards smelted in the pots of the smalt-furnaces with the addition of iron, carbon, and slag. Two layers are thus obtained, the upper one consisting of the cobalt-speiss, the lower being almost pure bismuth, which, owing to its low melting-point, can be drawn off in the liquid state after the upper layer of speiss has solidified. The crude bismuth thus obtained, only contains small traces of iron, cobalt, nickel, lead, silver, sulphur, and arsenic, and is purified by melting it on a slightly inclined iron plate, under which a wood fire is made, so that the bismuth melts and runs down. In this way almost chemically pure refined bismuth is obtained; it is then cast into semi-circular moulds in masses weighing from 10 to 12 kilos., and thus sent to market. In Freiberg, where ores of lead and silver containing bismuth are worked, the bismuth collects as an oxide in the refining of the silver in the slag or *blicksilber*. This often contains from 5 to 20 per cent. of bismuth, which is then extracted by solution in cold hydrochloric acid, and the solution diluted with water, until it becomes turbid. The liquors are allowed to stand till clear, and then a sufficient quantity of water added to precipitate the whole of the bismuth as basic salt. This is then fused with soda-ash and coal, and the fused metal cast into bars.

In Altenburg, bismuth is also obtained in the wet way from the roasted tin slags, and in France the ore occurring at Meymac is treated with hydrochloric acid, the bismuth precipitated by iron, and afterwards reduced by carbon. Bismuth was also formerly reduced at Joachimsthal, but now the ore is sent to Saxony to be smelted.

A considerable amount of foreign bismuth is worked up in England at the Magnesium Works at Patricroft. Some comes from Adelaide in South Australia, some from Bolivia and Peru. The ore there occurs very high up in the Andes. Thus one Peruvian ore containing 5 per cent. of tellurium occurs, according to David Forbes, at an elevation two-thirds that of Illampu, the highest point of the chain of 25,000 feet; and a bismuth sulphide containing antimony is found in Bolivia, at a height of 19,000 feet, near the mountain Chovolque in the province of Chichas.

The total production of bismuth amounts to about 25,000 kilograms per annum. Of this about 18,000 kilos. come from

Saxon works; 2,500 from Freiberg; 2,500 from England; 1,500 from Johanngeorgenstadt, and 500 from Altenberg. The quantity obtained in France from 1867 does not appear to amount to above a few hundreds of kilos. The composition of commercial bismuth is seen from the following table:

Analyses of Commercial Bismuth.

	Saxon Bismuth.	Bismuth from Joachimsthal.	Peruvian Bismuth.
Bismuth . .	99·77	99·32	93·37
Iron . . .	trace	trace	2·058
Copper . .	0·08	trace	
Lead . . .	—	0·30	—
Silver . . .	0·05	0·38	—
Antimony .	—	—	4·57
Tin . . .	—	—	
Sulphur . .	0·10	—	—

Bismuth which contains one or more per cent. of lead melts at a much lower temperature than pure bismuth. Such an impure metal exhibits on cooling the peculiarity that the solid crust of pure crystallized bismuth is seen to be broken through by drops of a liquid alloy. On the other hand, if bismuth contains silver, the portions which cool first contain most of the silver, whilst the liquid which remains is nearly pure bismuth.

548 *Native bismuth* is sometimes found nearly pure. Usually, however, it contains other metals alloyed with it, or it is mixed with a variety of ores. The table on the next page gives analyses of native bismuth.

When bismuth is required for pharmaceutical purposes it is necessary to separate traces of arsenic which it sometimes contains. For this purpose it is melted with nitre or other oxidizing agent. The same end may be attained by fusing it with cream of tartar in a carbon crucible, when an alloy of potassium and bismuth is formed. The potassium in this alloy oxidizes first, and the whole of the arsenic as well as a portion of the silver is oxidized at the same time. Herapath,[1] who found a small quantity of thallium in certain bismuth preparations, recom-

[1] *Pharmaceutical Journal*, iv. 302.

mends that the bismuth salts which are to be employed for medicinal purposes should be boiled with caustic soda solution, the residue well washed with water, dissolved in nitric acid, and the basic nitrate precipitated by the addition of an excess of water. From this the other preparations of the metal can be obtained.

Analyses of Native Bismuth.

Locality . .	Peru.		Dalekarlein in Sweden.	
Analyst . .	Genth.	Forbes.	Cleve.	Feilitzen.
Bismuth .	99·914	94·46	95·16	91·15
Iron . .	trace	—	1·80	4·03
Copper .	—	—	trace	trace
Gold . .	—	trace	—	—
Sulphur .	—	0·07	1·42	2·28
Tellurium .	0·042	5·09	—	—
Arsenic .	—	0·38	—	—
Silica . .	—	—	0·23	0·34

549 *Properties.* Bismuth is a hard brittle metal, having a bright metallic lustre, a greyish-white colour, with a distinctly reddish tinge. Its specific gravity at 12° is 9·823: it melts at 270°, and expands in the act of solidification. At a very high temperature it can be distilled in a current of hydrogen, and it volatilizes in the arc of a powerful battery. When a large quantity is melted, allowed slowly to cool until the surface begins to solidify, the crust then broken, and the liquid metal poured out, fine large crystals are obtained. These are obtuse rhombohedrons which have the appearance of cubes as their angles approach closely to 90°. They oxidize in the air, and frequently become covered with an iridescent film of oxide. The same colours may be obtained when the metal is melted in the air, but if the heat be continued, the metal gradually becomes altogether converted into oxide, and at a red-heat steam is slowly decomposed by bismuth. This metal combines also directly with the elements of the chlorine group, but hydrochloric and sulphuric acids do not act upon it in the cold.

The latter acid, however, dissolves it on heating, with evolution of sulphur dioxide. But the best solvents for bismuth are nitric acid and aqua-regia, both of which dissolve the metal readily in the cold.

550 *Fusible Metal.* Bismuth serves for the preparation of many pharmaceutical products and cosmetics. A considerable quantity is also employed in the preparation of fusible metal, the melting point of which can be altered according to the proportions of its constituents. The following table gives the composition and melting-point of some of these:

	Newton's Metal.	Rose's Metal.	Lichtenberg's Metal.	Wood's Metal.
Bismuth .	8	2	5	4
Lead . .	5	1	3	2
Tin . . .	3	1	2	1
Cadmium .	0	0	0	1
Melting-point	94°·5	93°·75	91°·6	60°·5

The melting-point can be still further reduced by the addition of mercury. Fusible metal is now largely used for stereotyping, obtaining copies of wood-cuts, &c., and is not only valuable on account of its low melting-point, but also because it expands considerably in the act of solidification, and thus giving a perfect cast, and it is important to make the cast when the metal is so far cooled that it is beginning to be viscid. If any of these liquid alloys be poured into a glass vessel, this flies to pieces when the metal cools. Bismuth is also used in the manufacture of solder, and the soldering can be effected under hot water when a few drops of hydrochloric acid have been added. Alloys of lead, tin, and bismuth mixed together in such proportion that the mixture fuses at some particular temperature above 100° serve as safety plugs for boilers. As soon as the steam reaches the pressure which corresponds to the melting-point, the plug gives way, and the steam escapes. Bismuth alloys, melting at a given temperature are used for tempering steel; the pencils used for writing on the so-called metallic paper likewise consist of an alloy of bismuth.

BISMUTH AND OXYGEN.

551 These elements unite together to form the following compounds:

Bismuth dioxide, Bi_2O_2.
Bismuth trioxide, Bi_2O_3.
Bismuth tetroxide, Bi_2O_4.
Bismuth pentoxide, Bi_2O_5.

Bismuth Dioxide, Bi_2O_2, is formed when the metal is heated not quite to its melting-point in the presence of air. It is obtained in a purer state when bismuth trioxide and tin dichloride are added together in molecular proportions, and the mixture dissolved in hydrochloric acid, the acid solution being poured into a tolerably concentrated solution of caustic potash. The brownish-black precipitate thus obtained is treated with concentrated caustic potash in order to separate the stannic acid, and then washed and dried at 100°. It is a greyish-black crystalline powder which, when heated in the air, burns like tinder.[1] It acts as a base, but its salts have been but slightly examined.

Bismuth Dichloride, $BiCl_2$, is formed when a slow current of chlorine is passed over the fused metal, or when the metal is heated with calomel to 250°. It is a black, crystalline, slightly volatile mass, which on heating in the air decomposes with separation of a portion of the metal, and formation of the trichloride and an oxychloride $Bi_4Cl_2O_3$ or $2BiCl_2 + 3Bi_2O_3$.

If the tribromide be fused with bismuth a mass of brown crystalline needles is obtained, which probably consists of the *dibromide*. These are decomposed by hydrochloric acid with separation of spongy bismuth.

In the process described for the preparation of the pure dioxide a stannate of this oxide is formed. This compound can best be obtained by pouring a solution of tin dichloride upon powdered nitrate of bismuth. It is a dark yellow powder.

[1] Schneider, *Pogg. Ann.* cxix. 331.

BISMUTH TRIOXIDE AND THE BISMUTH SALTS.

552 *Bismuth Trioxide*, Bi_2O_3, is found as bismuth ochre in Cornwall, Virginia, Siberia, and the Erzgebirge, as a yellow or greenish-grey amorphous mass or as a powder, and it usually contains ferric oxide and other impurities. In order to prepare it artificially, the hydroxide, carbonate, or nitrate is heated. Thus obtained, it is a yellow powder, having a specific gravity of 8·2, which fuses at a red-heat, forming a brown liquid solidifying to a yellow crystalline mass. When a boiling solution of a bismuth salt is precipitated with potash, the trioxide is obtained in microscopic needles, and if this be melted with caustic potash the product is found to crystallize in rhombic prisms. The oxide prepared by roasting the metal appears to have been employed as a yellow paint in Agricola's times. Bismuth has also been used for replacing lead in flint-glass or strass, as this possesses a much higher refractive index than ordinary flint-glass; if, at the same time, the potash be replaced by thallium, a glass is obtained whose refractive index is higher than that of any other kind.

Bismuth trioxide is a stronger base than the corresponding oxide of antimony, and forms a well-defined series of salts.

Bismuth Trihydroxide, $Bi(OH)_3$, is obtained as a white amorphous powder by precipitating a bismuth salt with cold caustic soda or ammonia.

Bismuth Trichloride, $BiCl_3$, was first prepared by Boyle[1] by heating bismuth with corrosive sublimate. It is also formed when the metal is burnt in a stream of chlorine, or when a concentrated solution of the oxide in hydrochloric acid is distilled and the receiver changed when all the water has come over. Bismuth trichloride is a granular white mass, easily fusible, and readily volatile, subliming in fine crystals, which melt at from 225° to 230°, and yielding a vapour having a specific gravity of 11·35 (Jaquelain). Heated in a current of hydrogen it is reduced to dichloride.[2] It forms a syrupy liquid when dissolved in a small quantity of water, though a larger quantity of water decomposes it, with formation of *bismuth oxychloride*, BiOCl,

[1] *Experiments and Considerations Touching Colours.*
[2] Muir, *Journ. Chem. Soc.* 1876, i. 144.

which is thrown down as a pure white powder, insoluble in water, though readily dissolved in acids. Heated in the air bismuth trichloride loses chlorine and takes up oxygen, but in absence of air it becomes yellow-coloured and fuses without decomposition.

When a solution of the oxide in an excess of hydrochloric acid is evaporated, fine needle-shaped crystals are deposited, having the composition $BiCl_3 + 2HCl$. Bismuth trichloride forms double salts with the chlorides of the alkali metals, and when the anhydrous chloride is treated with ammonia, three distinct compounds are obtained. One of these is a white, very volatile mass, having the formula $BiCl_3 + 3NH_3$; the two others remain behind in the retort in the process of preparation and have the composition $BiCl_3 + 2NH_3$ and $2BiCl_3 + NH_3$. The first of these forms a dirty-grey mass, whilst the second is red and crystalline. They combine with hydrochloric acid to form double salts, which are also obtained when sal-ammoniac is added to the solution of bismuth in the right proportion and the mixture evaporated.[1] When the dichloride is treated with chlorine a brownish-red powder is obtained of Bi_3Cl_8. This decomposes on heating into chlorine, trichloride, and dichloride.

553 *Bismuth Tribromide*, $BiBr_3$. When bromine vapour is passed over powdered bismuth an energetic reaction takes place and a red liquid volatilizes. This cools to a gold-yellow glistening deliquescent crystalline mass, which melts at from 210° to 215°. Bismuth tribromide crystallizes from ether in prisms, and water decomposes it into white insoluble oxybromide, BiOBr. It forms crystalline double salts, with the bromides of the alkali-metals, and with ammonia it forms compounds similar to the chloride.

Bismuth Tri-iodide, BiI_3, is obtained by heating the powdered metal with iodine, and heating the product. It sublimes in greyish-black metallic glistening tablets, which are not decomposed by cold water, though they are converted by hot water into an insoluble oxyiodide. If a solution of the iodide in hydriodic acid be evaporated rhombic pyramids of $BiI_3 + HI + 4H_2O$ are deposited. Bismuth iodide forms a large number of double salts, which have been investigated by Nicklès[2] and Linau.[3]

[1] Dehérain, *Compt. Rend.* liv. 924.
[2] *Compt. Rend.* l. 872, and *Journ. Pharm.* [3], xxxix. 116.
[3] *Pogg. Ann.* cxi. 240.

Bismuth Oxyiodide, BiOI, is obtained by decomposition of the tri-iodide with boiling water or by heating the same in the air, as a copper-red crystalline mass, which can be sublimed when heated in absence of air, but is gradually converted in presence of air into a crystalline oxide.

Bismuth Trifluoride, BiF_3, is obtained as a white powder by dissolving the oxide in hydrofluoric acid and evaporating the solution.

Bismuth Trisulphate, $Bi_2(SO_4)_3$, is obtained as an amorphous white mass by dissolving the metal or the oxides in concentrated sulphuric acid and evaporating. This salt is decomposed by water with formation of the basic salt, $Bi_2(OH)_4SO_4$. When this is heated it loses water, and on cooling a yellow mass, consisting of $(BiO)_2SO_4$ is obtained. This salt is also obtained by heating the other sulphates. Another of these basic salts has the composition $BiSO_4(OH) + H_2O$, and is obtained in small needles by acting upon the nitrate with sulphuric acid.

Bismuth Trinitrate, $Bi(NO_3)_3 + 3H_2O$, is obtained in large transparent triclinic prisms by dissolving the metal in nitric acid and evaporating the solution, which corrodes paper, and must, therefore, be filtered through asbestos or pounded glass. The crystals, which are deliquescent, are decomposed on heating, first losing their water, and then leaving a residue, first of basic salt, and lastly of the trioxide.

554 *Basic Bismuth Nitrate,* $Bi(OH)_2NO_3$. Libavius was aware that the solution of bismuth in nitric acid is precipitated by water, and Lemery, who describes the preparation of this compound, states that water containing common salt should be employed for this precipitation, pure water precipitating it, but much more slowly; and he adds that the product obtained weighs more than the metal employed. The reason of this, he explains, is that a certain quantity of spirit of nitre remains behind, even if the precipitate be well washed. Boyle states that the solution of bismuth in aqua-fortis is almost completely precipitated by common water. In spite of this, many chemists, looking at the analogy between lead and bismuth, believed that salt water was necessary for the precipitation; indeed the substance was for some time termed horn-bismuth. This error was definitely rectified by Pott, in 1739.

Basic nitrate of bismuth, formerly termed *magistery of bismuth,* is used as an important medicine, and many different receipts are given for its preparation. According to the British

Pharmacopœia, *bismuth subnitras* is first obtained by dissolving 2 parts by weight of bismuth in a mixture of 4 parts of nitric acid of specific gravity 1·42, diluted with 3 parts of water. The clear liquid is poured off from any insoluble matter, and evaporated to the point at which it occupies two volumes, and this is then poured into 80 parts of distilled water. The clear liquid is then decanted, and water added to the clear liquid; this is well stirred up, and the precipitate collected on a filter and dried at a temperature not higher than 55°. The German and French pharmacopœias recommend somewhat similar processes. In all these methods a considerable quantity of bismuth remains in solution, and this may be obtained, as the hydroxide, by precipitating with ammonia.

Basic bismuth nitrate is a crystalline powder which reddens moistened litmus paper. When heated to 100° it is converted into the compound $BiO(NO_3)_2(OH)_2$. Its composition varies somewhat, according to the quantity of water used in the preparation. When washed for a long time it becomes more basic, until at last the hydroxide is formed.

Basic nitrate of bismuth is largely used as a medicine in cases of chronic diarrhœa and cholera. The amount of this material employed in the French army amounts to 1,250 kilos per annum, most of which goes to Algiers. During the American war it was largely used in the field-hospitals for similar purposes, and its consumption in Germany has of late largely increased. It is also used in considerable quantities as a cosmetic; and this use of basic nitrate of bismuth is due to Lemery, who recommends it for softening the skin. When used for this purpose it was first termed *blanc d'Espagne*, which name, however, was used to designate many other white pigments. Another name for this cosmetic is *blanc de fard*.

The basic nitrate as well as the oxide is also used for giving a colourless iridescent glaze to porcelain. This is obtained by rubbing up basic nitrate with resin, and gently heating the mixture with lavender oil. It can be coloured by the addition of oxides, such as oxide of chromium, which gives to it a sulphur or lemon-yellow colour. With addition of 5 per cent. of gold to the oxide of bismuth a splendid copper-red colour with a reflected golden lustre is obtained. When a smaller quantity of this same substance is employed, the glass assumes a violet or pure blue colour, whilst with another treatment a

rose-red tint is obtained. These glazes are also used in glass-staining.

555 *Bismuth Orthophosphate*, $BiPO_4$, is precipitated when solutions of bismuth nitrate and phosphoric acid are brought together in presence of nitric acid. In the same way an insoluble *pyrophosphate*, $Bi_4(P_2O_7)_3$, is prepared with pyrophosphoric acid. When the oxide and phosphorus pentoxide are fused together a clear glass is obtained, which on slow cooling becomes crystal-, and probably consists of the tetrametaphosphate.

Bismuth Arsenate, $Bi_4(As_2O_7)_3$, is a white precipitate insoluble in water and nitric acid but soluble in hydrochloric acid.

Bismuth Silicate, $Bi_4(SiO_4)_3$, occurs as eulytine, found in small glistening yellow or brown regular tetrahedrons and occurring in the Erzgebirge together with phosphates of iron and manganese.

Basic Bismuth Carbonate, $2(BiO)_2CO_3 + H_2O$, is obtained as a white precipitate when carbonate of ammonia is poured into a solution of bismuth nitrate and dried at a gentle heat. It is employed as a medicine. At 100° it loses water, and when more strongly heated is readily converted into the trioxide.

The mineral bismutite is another basic carbonate, $3(BiO)_2CO_3 + 2Bi(OH)_3 + 3H_2O$. This is found at Schneeberg, at Chesterfield, South Carolina, and at other places, together with bismuth ores. It is a white or siskin-green earthy mass and sometimes occurs in acicular pseudomorph crystals.

Chromates of Bismuth. When normal potassium chromate is added to a solution of bismuth nitrate a lemon-yellow finely crystalline precipitate is thrown down having the composition $Bi_6Cr_2O_{15} = 2(BiO)_2CrO_4 + Bi_2O_3$. This compound does not fuse and is not decomposed on heating. When treated with a quantity of nitric acid insufficient to dissolve it, it is converted into $Bi_2Cr_2O_9 = (BiO)_2Cr_2O_7$; and this salt is also obtained by adding a solution of bismuth nitrate, as nearly as possible neutral, to an excess of a solution of potassium dichromate. It is an orange-yellow crystalline powder which decomposes on ignition and becomes of a dark-green colour. If a few drops of nitric acid be added to the liquid after precipitation and the whole boiled for a few hours, a cinnabar-red crystalline salt, $(BiO)_2CrO_4$, is thrown down, which on boiling with moderately strong nitric acid partially dissolves and is partially converted into ruby-red crystals having the formula $Bi_2Cr_4O_{15} + H_2O$.[1] Other polychromates of bismuth have been prepared.[2]

[1] Muir, *Journ. Chem. Soc.* 1876 [2], 12. [2] *Ibid.* 1877, i. 24 and 645.

BISMUTH PENTOXIDE AND BISMUTHIC ACID.

556 *Bismuth Pentoxide*, Bi_2O_5, is obtained as a brown powder by heating bismuthic acid to 130°. It is an extremely unstable compound and when heated loses oxygen, which gas is also given off on treatment with sulphuric acid, whilst chlorine is evolved when the substance is heated with hydrochloric acid.

Bismuthic Acid, $HBiO_3$, is obtained by passing a current of chlorine into a boiling solution of caustic potash containing bismuth trioxide in suspension. A red powder then separates out which is washed with dilute nitric acid and water. The same substance may be obtained by fusing caustic potash with a basic nitrate of bismuth in contact with the air until the mass has become dark-brown. On cooling, it is lixiviated with boiling water and the residue treated as above.

Metabismuthic Acid, $H_4Bi_2O_7$, is formed when a solution of the nitrate is precipitated with an excess of potassium cyanide.[1] It is a dark-brown powder which is distinguished from bismuthic acid inasmuch as it is decomposed at 150° with separation of water.

The salts of the bismuthic acids have been but very incompletely investigated. If common bismuthic acid be dissolved in boiling caustic potash and the solution concentrated, a red precipitate of $KBiO_3 + HBiO_3$ is thrown down (Arppe). This may perhaps be the tetrabismuthate, $K_2Bi_4O_{11} + H_2O$, but Muir was unable to obtain this compound. The following compound may be considered to be a salt of bismuthic acid.

Bismuth Tetroxide, $Bi_2O_4 = (BiO)BiO_3$, is formed when the trioxide is fused with alkalis in contact with the air or when it is treated with caustic potash and chlorine passed in until the mass becomes of a yellowish-red colour. On addition of nitric acid the yellowish-red hydrate is thrown down, $Bi_2O_4 + 2H_2O$.

BISMUTH AND SULPHUR.

557 *Bismuth Disulphide*, Bi_2S_2, is obtained as a grey metallic lustrous mass of needle-shaped crystals when the above elements are fused together in the proportion of their atomic weights and the mixture allowed to cool quickly. When a current of sulphuretted hydrogen is passed through a dilute alkaline solution

[1] Boedeker, *Ann. Chem. Pharm.* cxxiii. 61.

of bismuth nitrate free from air, mixed with tin dichloride, the dioxide which is first formed is converted into a black powder having the composition $Bi_2S_2 + 2H_2O$, which on trituration assumes a metallic lustre, and when this is treated with hydrochloric acid the following reaction takes place:—

$$3Bi_2S_2 + 12HCl = 2Bi + 4BiCl_3 + 6H_2S,$$

the bismuth separating out as a spongy mass.

Bismuth Trisulphide, Bi_2S_3, occurs as bismuthite in rhombic crystals, and also massive with a foliated or fibrous structure and having a specific gravity of 6·4. It is found at Brandy Gill, Carrock Fells in Cumberland, at Redruth and Botallack, and other localities in Cornwall, in the Erzgebirge, in Bolivia, and in other localities. It is obtained artificially by fusing the metal with an excess of sulphur, or by precipitating a solution of bismuth chloride with sulphuretted hydrogen. Thus prepared it forms a blackish-brown precipitate easily soluble in nitric acid and in boiling concentrated hydrochloric acid, but not in alkalis or their sulphides. When it is heated to 200° in a solution of the latter it becomes crystalline, assuming the form of bismuthite.

Bismuth Thioxysulphide, Bi_4O_3S, occurs as karelilinite, in a crystalline mass having a strongly metallic lustre and found at the Savodinck Mine in the Altai. If a mixture of 40 parts of sulphur and 142 parts of bismuth trioxide be heated to dark redness a grey crystalline mass of $Bi_6O_3S_4$ is formed.

Bismuth Chlorsulphide, BiSCl, is obtained by fusing together in the air 1 part of sulphur and 8 parts of ammonium bismuth chloride, or by heating the latter compound in a current of sulphuretted hydrogen. It forms white needles which are insoluble in water and dilute hydrochloric acid.

BISMUTH, SELENIUM, TELLURIUM, &c.

558 *Bismuth Triselenide*, Bi_2Se_3, is obtained by fusing the elements together as a metallic lustrous brittle crystalline mass, having a specific gravity of 6·82, and which is attacked only by nitric acid and aqua regia.

Bismuth Tritelluride, Bi_2Te_3, occurs as tetradymite in metallic pale steel-grey rhombohedrons, or in foliated or granular masses having a specific gravity of 7·2 to 7·9. It is found in Transylvania, Hungary, Sweden, Norway, and in several localities in the United States, together with other

tellurium ores. In some varieties of this mineral a portion of the tellurium is replaced by sulphur and selenium, although the analyses of the pure material correspond to the above formula. G. Rose and P. Groth[1] consider this mineral to be an isomorphous mixture of the elements, as it is not isomorphous with bismuthine, and as bismuth and tellurium can be fused together in all proportions.

Phosphorus and *arsenic* do not readily combine with bismuth. The first of these forms a compound with molten bismuth, and if a current of phosphuretted hydrogen be passed through a solution of bismuth, a black phosphide is precipitated, which, however, decomposes in absence of air into its elements. An alloy of bismuth and arsenic gives up the whole of the latter when heated. Arseniuretted hydrogen produces a black precipitate in bismuth solutions which behaves in a precisely similar way.

Detection and Estimation of Bismuth.

559 When a bismuth compound is heated in the upper reduction-flame of the Bunsen burner on an asbestos thread, a cold porcelain dish, held above it, receives a brown or black deposit of metallic bismuth, which is only slowly dissolved in cold dilute nitric acid. A brittle metallic bead is obtained when the compound is heated on the carbonized match, and this dissolves in nitric acid, yielding a brown precipitate of bismuth dioxide with stannous chloride and caustic soda. A characteristic reaction of the bismuth salts is the precipitation of the blackish-brown sulphide with sulphuretted hydrogen, insoluble in sulphide of ammonium, and easily soluble in nitric acid. In addition to this, water produces, in solutions which are not too strongly acid, a white precipitate of an insoluble basic salt, and ammonia throws down a white precipitate of the hydroxide insoluble in excess. These reactions serve to separate bismuth from other metals, as well as to detect its presence. If other metals precipitable by sulphuretted hydrogen be present, the washed precipitate is first digested with sulphide of ammonium, in order to separate arsenic, antimony, and tin. The precipitate is then well washed, dissolved in nitric acid, and dilute sulphuric acid added to the filtrate to separate lead; the precipitate filtered off, and an excess of ammonia added which

[1] *Tabell. Uebersicht. d. Einf. Mineralien*, 73.

throws down the bismuth as the hydroxide, whilst any copper or cadmium present remains in solution. The precipitate is dissolved in a small quantity of hydrochloric acid, the liquid concentrated by evaporation, and added to a large quantity of water, when the insoluble oxychloride is precipitated.

Care, however, must be taken that the whole of the antimony is previously removed by a long digestion of the sulphides with sulphide of ammonium, and the residue well washed with water, for otherwise an insoluble oxychloride of antimony may be precipitated, and this may be mistaken for bismuth.

Bismuth can be determined *quantitatively* in several ways. If the solution consist only of nitrate, it may be precipitated with carbonate of ammonia, heated for some time almost to boiling, filtered, the precipitate dried and converted by ignition into the trioxide which is weighed. If other acids are present, the bismuth is precipitated by sulphuretted hydrogen, the washed precipitate dissolved in nitric acid and treated as above, or it may be dried, any excess of sulphur got rid of by carbon disulphide, and the residual pure sulphide dried at 100°. Bismuth may also be estimated as the metal by reduction with cyanide of potassium. The metallic mass is well washed with water and alcohol, and weighed after drying. Lastly, if the solution of the nitrate contains only a small quantity of free acid, it may be precipitated with potassium dichromate, or with arsenic acid, and the precipitate dried and weighed.

The *atomic weight* of bismuth was first determined by Gmelin,[1] and afterwards by Schneider,[2] by converting the metal into the trioxide. Their results give the number 207·5, whilst Dumas[3] by the analysis of the chloride, arrived at the number 210. This latter number is probably the most exact, inasmuch as the differences in the atomic weights of analogous elements, already alluded to, thus become nearly constant:

In = 113·4.	Sn = 117·8.	Sb = 122.
Tl = 203·6.	Pb = 206·4.	Bi = 210.

TANTALUM, Ta = 182.

560 This metal is so closely connected with the next one, niobium, that it will be most convenient to consider their history together.

[1] *Handbook*, iv. 428. [2] *Pogg. Ann.* lxxxii. 303.
[3] *Ann. Chim. Phys.* [3], lv. 177.

In the year 1801, Hatchett [1] laid before the Royal Society an investigation on a mineral from Massachusetts, which he believed to contain a new metal, to which he gave the name of columbium. In the following year, Ekeberg,[2] in Sweden, investigating the yttrium minerals, discovered a new element in a mineral to which he afterwards gave the name of yttrotantalite, whilst the same element also occurred in a mineral termed tantalite. In consequence of this he named the metal *tantalum*, partly because mythological names were frequently used, and partly also as pointing to the fact "that when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them."

In 1809, Wollaston [3] endeavoured to show that columbium and tantalum were identical, and a few years later Berzelius [4] more carefully investigated the oxides of the last-named metal prepared from tantalite, and prepared tantalic acid. Afterwards, in 1839, Wöhler [5] found that the acid-forming oxide contained in pyrochlor and in the Bavarian tantalites possesses peculiar properties; and Rose [6] then observed that the columbites of Bodenmais contained the oxide of a new metal, to which he gave the name of niobium, and in 1846 he thought that he found a third new metal, to which he gave the name of pelopium. In 1853 he came to the conclusion on further investigation that niobic acid and pelopic acid were different oxides of niobium, and to the first of these he gave the name of niobic acid, whilst the latter was designated as hyponiobic acid. These, however, exhibited "a relationship so peculiar that the whole range of chemistry does not furnish an example of a similar kind." [7] In 1856-7, Hermann observed that niobium and tantalum usually occur together, whilst in 1864-5, Blomstrand [8] showed that Rose's hyponiobic chloride contained oxygen, and is an oxychloride, and Marignac [9] almost at the same time proved that the double salts which hyponiobic fluoride forms with metallic fluorides, are isomorphous with similar double salts containing titanium fluoride, TiF_4, and tungsten oxyfluoride, WO_2F_2. Inasmuch as the sum of the atoms in all these isomorphous compounds is constant, and as, according to analysis, the hyponiobic fluoride contained three atoms of

[1] *Phil. Trans.* 1802, 49.
[2] *Ann. de Chim.* xliii. 276.
[3] *Phil. Trans.* 1809, 246.
[4] *Pogg. Ann.* iv. 6.
[5] *Pogg. Ann.* xlviii. 91.
[6] *Ibid.* lxiii. 307, 693; lxix. 118.
[7] *Ibid.* xc. 471.
[8] *Journ. Pract. Chem.* xcvii. 37.
[9] *Ann. Chim. Phys.* [4], viii. 5, 49.

fluorine, Marignac concluded that it must be an oxyfluoride of the composition, $NbOF_3$ and he succeeded in obtaining experimental evidence of the truth of this view. At the same time he showed that the tantalic acid, which up to that time had been supposed to be analogous to titanic acid, and to which the formula TaO_2 had been given, must, like the highest oxide of niobium, be a pentoxide, as these two oxides occur in isomorphous mixture in several minerals, and as both metals form isomorphous double fluorides as K_2TaF_7 and K_2NbF_7.

The truth of this view of the composition of the niobium and tantalum compounds was confirmed by the experiments of Deville and Troost,[1] who in 1865 determined the vapour densities of niobium chloride, niobium oxychloride, and tantalum chloride, which were found to correspond to the formulæ $NbCl_5$, $NbOCl_3$, and $TaCl_5$. The investigation of Blomstrand and Marignac next showed that the metal dianium, supposed by v. Kobell to be contained in various columbites, is in fact identical with niobium, and Marignac further showed that ilmenium which Hermann believed he had discovered in samarscite, is a mixture of niobium and tantalum. Its discoverer, however, still adheres to his belief in the existence of ilmenium, and quite recently he is said to have found another metal to which he gives the name of neptunium. His views do not, however, meet with general acceptance.

561 Tantalum and niobium are found in many other minerals in addition to those already mentioned. The following table gives the composition of some of the more important of these.

Tantalite (*analysed by Rammelsberg*).

Locality . . .	Finland.	Sweden.
Ta_2O_5	76·34	49·64
Nb_2O_5	7·54	29·27
SnO_2	0·70	2·49
FeO	13·90	13·77
MnO	1·42	2·88
	99·90	98·05

[1] *Comptes Rendus*, lx. 1221.

Columbite (*analysed by Blomstrand*).

Locality . . .	Greenland.	Massachusetts.	Bodenmais.
Ta_2O_5 . . .	—	28·55	22·79
Nb_2O_5 . . .	77·97	51·53	56·43
WO_3 . . .	0·13	0·76	1·07
SnO_2 . . .	0·73	0·34	0·58
FeO	17·33	13·54	15·82
MnO . . .	3·28	4·55	2·39
ZrO_2 . . .	0·13	0·34	0·28
MgO . . .	0·23	0·42	0·40
PbO . . .	0·12	—	—
H_2O . . .	—	0·16	0·35
	99·92	100·19	100·11

Pyrochlor (*analysed by Rammelsberg*).

Locality	Siberia.	Kaiserstuhl.
Nb_2O_5	51·19	47·13
TiO_2	10·47	13·52
ThO_2	7·56	—
Ce_2O_3	7·00	7·30
CaO	14·21	15·94
MgO	0·22	0·19
FeO	1·84	10·03
Na_2O	3·71	3·12
F	3·06	2·90
	101·26	100·13

Yttrotantalite, Fergusonite, Euxenite (analysed by Rammelsberg).

	Yttrotantalite.	Fergusonite.	Euxenite.
Locality. . .	Ytterby.	Greenland.	Arendal.
Ta_2O_5 . .	10·05	6·40	—
Nb_2O_5 . .	42·12	45·13	35·83 ?
WO_3 . . .	0·22	0·15	—
SnO_2 . . .	0·24	0·48	24·33
Y_2O_3 . . .	27·69	25·25	17·23
Er_2O_3 . .	12·44	9·76 ?	9·39
Ce_2O_3 . .	1·90	2·05	2·34
CaO . . .	3·21	0·61	—
FeO . . .	0·63	0·74	3·61
UO_2 . . .	1·26	2·62	8·86
	99·76	96·10	101·59

Besides occurring in these minerals, tantalum is frequently found in small quantities in tinstone, wolfram, pitchblende, and other minerals.

562 For the purpose of preparing the tantalum compounds, tantalite, or some other mineral containing this metal, is finely powdered and fused with three times its weight of acid potassium sulphate, the fused mass completely boiled out with water, and the residue digested with sulphide of ammonium, in order to remove tin and tungsten, the iron present being at the same time converted into sulphide. The residue is washed and boiled with concentrated hydrochloric acid, when tantalum hydroxide remains behind, and this is then washed with boiling water and ignited. The oxide thus obtained usually contains silica and niobic acid. The former is removed by dissolving in hydrofluoric acid, and evaporating with sulphuric acid; the latter by adding to the boiling hydrofluoric acid solution 1 part of potassium fluoride to every 4 parts of the oxide present, and concentrating the solution until 1 gram of the oxide is contained in 7 cc. of the solution. On cooling, fine needle-shaped crystals of potassium tantalofluoride separate

out. These are washed with water until the wash-water after standing for two hours does not give an orange-red precipitate, but a sulphur-yellow one with tincture of galls. On evaporating the mother-liquor and the wash-water, more of the salt is obtained, which at last is mixed with scales of the niobium salt. The pure potassium tantalofluoride is then mixed with its own weight of concentrated sulphuric acid and heated gradually to 400°, and the residue boiled out with water, when a granular crystalline compound of tantalum oxide and sulphuric acid remains behind. This is decomposed on ignition, and it is advisable to add carbonate of ammonia in order to get rid of the whole of the sulphuric acid.

Pure tantalum does not appear to have been prepared. Probably that got by Berzelius was the purest form that has yet been seen. This he obtained by igniting potassium fluotantalate with potassium. It is a black powder which assumes an iron-grey metallic lustre under the burnisher, and when gently heated takes fire in the air and burns to oxide. It dissolves in hydrofluoric acid with evolution of hydrogen, but in no other acids, not even in aqua-regia. Heated gently in chlorine, it burns brightly, and it also takes fire when heated in sulphur vapour.

TANTALUM AND OXYGEN.

563 *Tantalum Tetroxide*, Ta_2O_4, is formed when the pentoxide is heated in a very small carbon crucible, exposed to the highest heat of a wind furnace. It is a porous dark-grey mass which scratches glass, and when rubbed on a hone has a steel-grey colour. It gives a dark brown non-metallic powder, and is not attacked by acids even by a mixture of hydrofluoric and nitric acids, but burns when heated with formation of the pentoxide.

Tantalum Pentoxide, Ta_2O_5. The preparation of this body has already been described. It is a white amorphous infusible powder which when strongly heated becomes crystalline, and if ignited with boron trioxide or melted with microcosmic salt in a porcelain furnace it is obtained crystalline in rhombic prisms. When gently heated it has a specific gravity of 7·35, which after exposure to a white heat rises to 8·01. It does not dissolve in any acid, but volatilizes completely when ignited with ammonium fluoride.

Tantalum Hydroxide or Tantalic Acid, $HTaO_3$, is obtained in the form of a gelatinous mass, when the chloride is quickly mixed with water. If, however, the same compound be exposed to moist air until it is decomposed, and then mixed with water containing ammonia, the hydroxide is obtained as a crystalline powder, which when dried at 100° possesses the above composition, and is converted, with vivid incandescence, into pentoxide when heated to low redness. The hydroxide obtained by ignition with acid potassium sulphate does not exhibit this phenomenon. Tantalic acid dissolves in binoxalate of potash, in hydrofluoric acid, and, when in the nascent condition, in other acids.

TANTALATES.

564 The normal tantalates, to which class the tantalum minerals belong, are all insoluble in water. Besides these, others are known, derived from the unknown hydrate, hextantalic acid, $H_8Ta_6O_{19}$, of which only the compounds of the alkali-metals are soluble in water.

Potassium Hextantalate, $K_8Ta_6O_{19} + 16H_2O$, is formed by dissolving the acid in caustic potash, and also by fusing the pentoxide with double its weight of caustic potash. The fused mass is dissolved in water and allowed to evaporate in a vacuum. Transparent glistening monoclinic crystals are thus obtained which dissolve in lukewarm water without decomposition On boiling or evaporating in the air salts containing more tantalum are formed. If it is frequently ignited with sal-ammoniac and washed with water the normal salt, $KTaO_3$, is obtained.

Sodium Hextantalate, $Na_8Ta_6O_{19} + 25H_2O$, is obtained in a similar way to the potassium salt, a vivid incandescence occurring when the mixture is heated to redness. The fused mass is treated with water, the residue dissolved in hot water, and either allowed to cool or, inasmuch as it is insoluble in caustic soda, it is poured on to the top of a strong solution of this substance. It crystallizes in small hexagonal tables which dissolve at 13°·5 in 493, and at 100° in 162 parts of water. It is not decomposed by boiling water, and if the aqueous solution is mixed with alcohol, a precipitate of $NaTaO_3 + H_2O$ is formed, and this becomes anhydrous on ignition. The anhydrous salt is also formed by the ignition of the hextantalate.

Ammonium Tritantalate, $2NH_4Ta_3O_8 + 5H_2O$. This salt is

produced by the addition of sal-ammoniac to a solution of the sodium salt, and is a precipitate resembling chloride of silver. It is slightly soluble in water.

When tantalum pentoxide is strongly ignited with the chlorides of calcium, magnesium and other metals, crystalline tantalates of these metals are obtained.[1]

HALOID COMPOUNDS OF TANTALUM.

565 *Tantalum Chloride*, $TaCl_5$, is obtained by heating an intimate mixture of the pentoxide and carbon in a current of chlorine. It forms light-yellow needles and prisms which melt at 211° and boil at 242°, but begin to volatilize at so low a temperature as 144°, and may be readily sublimed in a current of carbon dioxide or chlorine. The specific gravity of the vapour, according to Deville and Troost, is 12·8, the calculated density being 12·42. It fumes in the air, and is converted into tantalic acid.

Tantalum Pentabromide, $TaBr_5$, is prepared in a similar way to the chloride, and exhibits properties closely resembling this compound.

Tantalum and iodine do not combine.

Tantalum Pentafluoride, TaF_5, is only known in solution. If this be evaporated even at a moderate temperature some of the fluoride volatilizes whilst tantalic acid remains behind. Tantalum fluoride forms double salts with the other metallic fluorides.

566 *Potassium Tantalofluoride*, K_2TaF_7. The mode of preparing this salt has been already described. It forms small rhombic needles which readily melt, but it does not decompose when ignited even to whiteness in a platinum vessel. It is easily soluble in hot, though sparingly so in cold water. When the solution is boiled for some time decomposition takes place, a white powder of the oxyfluoride, $K_4Ta_4O_5F_{14} = 4KF + 2TaF_5 + Ta_2O_5$, separating out. This reaction serves to detect the smallest quantity of tantalum when present together with niobium oxyfluoride (Marignac).

Sodium Tantalofluoride, $Na_2TaF_7 + H_2O$, is obtained by a process similar to that of the potassium salt, or by dissolving sodium hextantalate in hydrofluoric acid. On evaporation indistinct crystals of Na_3TaF_8, separate out, and then eight-sided rhombic tables of the above salt, which lose their water under 100°.

[1] Joly, *Compt. Rend.* lxxxi. 266 and 1266.

Ammonium Tantalofluoride, $(NH_4)_2TaF_7$. This is produced when ammonia is added to a hydrofluoric acid solution of tantalic acid, until a precipitate begins to form, the solution then being evaporated. It crystallizes in thin quadratic scales or needles which are easily soluble in water.

When tantalic acid is dissolved in an acid solution of ammonium fluoride, regular octohedrons are obtained on evaporation which have the composition, $3NH_4F + TaOF_3$.

TANTALUM AND SULPHUR.

567 *Tantalum Tetrasulphide*, Ta_2S_4, is obtained by acting upon white hot tantalum pentoxide, with a mixture of hydrogen and the vapour of carbon disulphide. It is a grey finely-granular friable mass, which may be pressed into masses resembling graphite, and these on burnishing possess the colour of brass. It is also formed when the chloride is ignited in a stream of sulphuretted hydrogen, and is thus obtained in crusts resembling pyrites in appearance. It is not attacked by hydrochloric acid even on boiling, and nitric acid and aqua-regia oxidize it but slowly.

TANTALUM AND NITROGEN.

When tantalum chloride is heated in ammonia gas to a temperature not above the point of volatilization of the sal-ammoniac which is formed, an amorphous yellowish-red mass of Ta_3N_5 is obtained. If the temperature then be raised to redness black tantalum nitride, TaN, is obtained, and this exhibits a metallic lustre when burnished. H. Rose, who first obtained this compound, believed it to be the metal.

Detection and Estimation of Tantalum.

568 In order to detect tantalum in a mineral, tantalic acid must be prepared from it, and this converted into a soluble tantalate. If ferrocyanide of potassium be added to this solution, a characteristic yellow precipitate falls down, and under the same circumstances tincture of galls likewise produces a bright yellow precipitate. The tantalum compounds do not colour a bead of borax or of microcosmic salt.

Tantalum is determined *quantitatively*, either as the pent-oxide or as potassium tantalofluoride. For further information on this point see the Niobium Compounds.

The *atomic weight* of tantalum was determined by Marignac [1] by the analysis of the potassium and ammonium tantalofluorides.

NIOBIUM, Nb = 94.

569 The history of this metal is given under Tantalum. The metal was first obtained by Blomstrand,[2] by reducing the chloride in hydrogen, as a mirror-like deposit on the tube, but it was not certain whether this was the pure metal or a hydride. Roscoe [3] obtained it in the form of a steel-grey crust, by passing the vapour of the pure chloride together with hydrogen repeatedly through a red-hot tube; this was then more strongly heated in a porcelain tube, through which hydrogen was passed. The metal contained only 0·27 per cent. of hydrogen as well as a small quantity of chloride and oxide, the latter being derived from diffused air. At 15°·5 it has a specific gravity of 4·06. It takes fire at a low temperature when heated in the air, oxidising with vivid incandescence, and also burns in chlorine when slightly warmed. It is hardly attacked by hydrochloric or nitric acid or aqua-regia even when heated, but dissolves in concentrated sulphuric acid, yielding a colourless liquid.

NIOBIUM AND OXYGEN.

570 *Niobium Dioxide*, Nb_2O_2, is formed when dry potassium niobium oxyfluoride is heated with sodium under a layer of potassium chloride over a gas blow-pipe. The fused mass is boiled with water, and the residue washed with water and afterwards with dilute alcohol. It then forms a white powder which on heating in the air oxidises with vivid incandescence. When gently warmed in chlorine gas it burns with formation of oxychloride, and it dissolves in the moist state in hydrochloric acid with evolution of hydrogen. If the vapour of the oxychloride be passed over heated magnesium wire, the same

[1] *Ann. Chim. Phys.* [4], ix. 251. [2] *Journ Pract. Chem.* xcvii. 37.
[3] *Mem. Manch. Lit. and Phil. Soc.* [3] vi. 186.

compound is formed in crystals which probably belong to the regular system.

Niobium Tetroxide, Nb_2O_4, is obtained as a heavy black powder, which appears blue by reflected light, by heating the pentoxide very strongly in hydrogen. It is not attacked by acids and burns in the air when heated to redness.

Niobium Pentoxide, Nb_2O_5. This compound is obtained in a similar way to tantalum pentoxide. It is best for this purpose to employ Greenland columbite which is converted into potassium niobfluoride, this is purified by repeated crystallisation, and then treated as has been described under the corresponding tantalum salt. It is a white amorphous infusible powder having a specific gravity of 4·53, which becomes crystalline when strongly heated. It may be obtained in prismatic crystals on fusion with boron trioxide or borax.

Niobium Hydroxide or *Niobic Acid*, $HNbO_3$, is formed by the decomposition of the oxychloride or pentachloride in moist air or by water. It is a white powder which, when dried at 100°, retains varying quantities of water, and in general possesses properties analogous to those of tantalic acid. It is only slightly soluble in hot hydrochloric acid, but the residue, after this treatment, can be dissolved in water. On the addition of zinc the solution becomes blue and a hydrated precipitate, probably of Nb_2O_4, separates out. The solution of niobic acid obtained by treatment with hydrochloric acid gives on the other hand a brown colour with zinc, and a brown oxide separates out which has the composition $Nb_3O_5 = Nb_2O_2 + 2Nb_2O_4$. Niobic acid is easily soluble in caustic alkalis and their carbonates.

NIOBATES.

571 *Potassium Hexniobate*, $K_8Nb_6O_{19} + 16H_2O$, is prepared by fusing the pentoxide with double its weight of carbonate of potash, dissolving in water, and evaporating in a vacuum. It forms large glistening monoclinic crystals which effloresce on exposure to air. If caustic potash be added to this solution and the mixture slowly evaporated, fine rhombic pyramids of $K_6Nb_4O_{13} + 13H_2O$ are deposited, and these effloresce quickly on exposure.[1]

When equal molecules of niobium pentoxide and potassium

[1] Marignac, *Ann. Chim. Phys.* [4] viii. 20.

carbonate are fused together, a distinctly crystalline mass is obtained, which, when treated with water, yields the salt $2K_2Nb_4O_{11} + 11H_2O$. If, however, a larger quantity of carbonate of potash be employed, the compound $K_4Nb_2O_7 + 11H_2O$ is obtained.[1]

The crystallised sodium niobates described by Rose were prepared from a mixture of the oxides of niobium and tantalum. According to Marignac, these crystallise indistinctly, and appear to be mixtures. The niobates of the metals of the other groups have been prepared by Joly, and correspond closely to the tantalates.

HALOID COMPOUNDS OF NIOBIUM.

572 *Niobium Trichloride*, $NbCl_3$, is obtained when the vapour of the pentachloride is slowly passed through a red-hot glass tube. It forms either crystalline crusts which have the appearance of iodine, or is found crystallised in long needles which are dichroic. It is neither volatile nor deliquescent; is not decomposed by water or ammonia, but is easily oxidized by nitric acid. When heated in the air it emits thick vapours, and when ignited in a current of carbon dioxide it forms niobium oxychloride, $NbOCl_3$, and carbon monoxide, a reaction which is not exhibited by any other metallic chloride (Roscoe).

Niobium Pentachloride, $NbCl_5$. When an intimate mixture of niobium pentoxide and a large excess of sugar charcoal is heated in a current of chloride perfectly free from air, yellow needles of the above compound are formed. These fuse at 194°, and boil at 240°·5, but begin to sublime at 125°. The yellow vapour has a specific gravity of 9·6 (Deville and Troost), the formula requiring 9·38. It dissolves in hydrochloric acid, forming a liquid, which gelatinises on standing, and when diluted with water or on boiling almost all the niobic acid separates out. Metallic zinc brought into the solution turns it a deep blue colour.

Niobium Oxychloride, or *Niobyl Chloride*, $NbOCl_3$, is formed by the direct union of the dioxide with chlorine, and also when a mixture of pentoxide with a small quantity of carbon is heated in chlorine. It is likewise formed by repeatedly distilling the pentachloride in a current of carbon dioxide over ignited pentoxide.

[1] Sautesson, *Bull. Soc. Chim.* [2] xxiv. 53.

It is a colourless fibrous crystalline mass, which volatilises without melting at about 400°, giving rise to a colourless vapour, of which the specific gravity was determined by Deville and Troost to be 7·88, theory requiring 7·48. When heated in carbon dioxide, and still more readily in hydrogen, it decomposes into pentoxide and pentachloride. It deliquesces on exposure to moist air, with formation of crystallised niobic acid, whilst when brought into contact with water it decomposes violently, forming amorphous niobic acid.

Niobium Pentabromide, $NbBr_5$, is prepared in the same way as the chloride, and is a purple-red mass, which on heating becomes yellow and volatilises.

Niobium Oxybromide, $NbOBr_3$. When a mixture of pentoxide and double its weight of carbon is heated in bromine vapour a yellow voluminous mass is obtained, which sublimes without fusion, and when heated in carbon dioxide is converted into the pentoxide.

Niobium Pentafluoride, NbF_5. This substance, like the fluoride of tantalum, is only known in solution, and possesses analogous properties to the latter compound.

573 *Niobium Oxyfluoride*, $NbOF_3$, is obtained by igniting a mixture of pentoxide and fluor-spar in a current of hydrochloric acid, in the form of small crystals, closely resembling zirconium fluoride. It forms double salts with other metallic fluorides, of which those of potassium and ammonium have been investigated by Marignac, who has prepared the following:

$(KF)_2NbOF_3 + H_2O$.	$(NH_4F)_2NbOF_3$.
$(KF)_3NbOF_3$.	$(NH_4F)_3NbOF_3$.
$(KF)_5(NbOF_3)_3 + H_2O$.	$(NH_4F)_5(NbOF_3)_3 + H_2O$.
$(KF)_4(NbOF_3)_3 + 2H_2O$.	NH_4FNbOF_3.
$HF(KF)_3NbOF_3$.	$(NH_4F)_3NbOF_3NbF_5$.

These are crystallisable, and are formed by dissolving niobic acid in a larger or smaller quantity of hydrofluoric acid, and adding the other fluorides in various proportions. The first salts of the two series, which Marignac terms normal salts, are those which are readily formed. The normal potassium salt is formed whenever the others are re-crystallised, and is deposited in the form of thin monoclinic scales isomorphous with potassium tungsten oxyfluoride, $(KF)_2WO_2F_2$, and with potassium titanium fluoride, K_2TiF_6. By dissolving this in hot hydrofluoric acid *potassium niob-fluoride*, K_2NbF_7, is formed,

which deposits in glistening rhombic needles. The normal ammonium salt crystallizes in rhombic tablets, and is isomorphous with ammonium tungsten oxyfluoride, $(NH_4F)_2WO_2F_2$.

NIOBIUM AND SULPHUR.

574 *Niobium Oxysulphide*, $NbOS_3$, is formed when carbon dioxide mixed with the vapour of disulphide of carbon is passed over the white-hot pentoxide. It is a black or brass-coloured crystalline powder. The same compound is easily formed, as a black woolly mass by heating the oxychloride in sulphuretted hydrogen. This powder, when rubbed in an agate mortar, attains a steely lustre, and when heated burns in the air with formation of pentoxide.

NIOBIUM AND NITROGEN.

When niobium pentoxide is heated to whiteness in ammonia it loses the half of its oxygen, and forms a black powder containing nitrogen. If niobium oxychloride be treated with dry ammonia, it becomes hot and turns yellow. This, when heated, gives off sal-ammoniac, and a black powder remains behind, which, when melted with caustic potash, yields ammonia in large quantity, and on heating in the air burns with incandescence. It is not attacked either by boiling nitric acid or aqua-regia, but dissolves readily in a mixture of hydrofluoric and nitric acids.

Detection and Estimation of Niobium.

575 The solution of a niobate yields with potassium ferrocyanide and hydrochloric acid a deep brown precipitate. Under some circumstances tincture of galls or tannic acid gives an orange-red precipitate. When zinc is added to the acidified solution the whole becomes blue and afterwards brown. Microcosmic salt or borax easily dissolves the pentoxide, and a bead is obtained which becomes violet, blue, or brown, in the reducing flame and red on the addition of ferric oxide.

The *quantitative* determination and separation of niobium is best understood from the following description of Rose's method.

given by Rammelsberg, for the analysis of tantalites and columbites.[1] The mixture of oxides obtained by fusion with acid potassium sulphate and lixiviation with water, is fused with sulphur and sodium carbonate, the fused mass treated with water, when any tin sulphide or tungsten sulphide which may be present is dissolved. The residual oxides of tantalum and niobium are then treated with dilute sulphuric acid in order to remove the iron, and again fused with acid potassium sulphate, and the oxides separated out by boiling the mass with water, whilst any iron, manganese, zinc, copper, or tin which may still be present is found in solution.

In order to separate niobium from tantalum the purified oxides are fused with potassium fluoride, the mass digested with a large quantity of water, and the solution boiled after addition of some hydrofluoric acid. On cooling, the largest portion of the tantalum separates out chiefly as tantalofluoride. The filtrate is evaporated to two-thirds its bulk, allowed to stand twenty-four hours in the cold, and the rest of the salt thus obtained. Sometimes a third evaporation of the filtrate is necessary. The potassium tantalofluoride can then be weighed, but it generally contains some iron which must be separated by heating with sulphuric acid, the purified tantalum being weighed as the pentoxide.

The solution which contains the niobium is also evaporated with sulphuric acid, the residue ignited and well washed with water, and again ignited, when niobium pentoxide remains behind. This may still contain a trace of titanium. In order to free it from this metal the fluo-double-salts are warmed with hydrochloric acid and zinc, when the titanium compound is reduced, and its amount estimated by volumetric analysis with potassium permanganate.

The *atomic weight* of niobium was determined by Marignac[2] to be 94, from numerous analyses of potassium niobium oxyfluoride.

[1] *Pogg. Ann.* cxliv. 56. [2] *Ann. Chim. Phys.* [4], viii. 16.

METALS OF THE GOLD GROUP.

Gold.	Palladium.	Ruthenium.
Platinum.	Rhodium.	Osmium.
	Iridium.	

576 The above metals may be divided into three classes according to their different behaviour with oxygen.

(1) Gold and platinum do not combine directly with oxygen under any circumstances.

(2) Palladium, rhodium, and iridium oxidise when they are heated in the air or oxygen, but their oxides decompose on strong ignition into metal and oxygen.

(3) Ruthenium and osmium unite with oxygen to form volatile oxides which do not undergo decomposition even at the highest temperatures.

Gold and silver were in former times classed by themselves as the noble metals. Afterwards platinum and the other metals of this group, which do not unite directly with oxygen, were likewise included under this term. The lower oxides of this group of metals act as weak bases; the higher ones on the other hand assume the character of acid-forming oxides. The gold group is connected with the iron group of metals inasmuch as many of its members form compounds resembling the cobalt-amines and the double cyanides of iron.

GOLD (AURUM) Au, = 196·2.

577 Of all the metals gold was probably the first to attract the attention of man, its occurrence in the native state, its brilliant lustre and its unalterability rendering it an object of value from very early times.

Metallic gold is mentioned in the Old Testament and in Homer, and the various names by which it is designated denote lustre or fine colour. Thus the Hebrew *zaháb*, the root of which signifies to glitter; whilst the Greek word χρυσός probably derived from the Sanscrit *hiranya* also signifies to glitter or flame. Our word "gold" probably is connected with *jvalita*, which also occurs in Sanscrit and which is derived from *jval* which also means to shine. As being the most perfect of the metals gold was compared by the alchemists to the sun; to it was

attributed the most singular virtues, and strenuous efforts were directed to the transmutation of the baser metals into ☉ (Sol).[1]

Gold is usually found in the native state, but never perfectly pure, being always alloyed with more or less silver. If it contain more than 36 per cent. of the latter metal it is termed *electrum*. Native gold usually also contains traces of iron and copper, as well as some of the other metals of the present group. An amalgam of gold also occurs in nature. Gold is likewise found in the following combinations: bismuth-aurite, Au_2Bi; calaverite, $AuTe_2$; sylvanite or graphic tellurium, $(AuAg)_2Te_3$; nagyagite or black tellurium, $(PbAu)_2(TeSSb)_3$. Traces of gold occur in many pyrites, blendes, and other ores. It has also been found in sea-water.

Native gold is generally found *in situ* in quartz-veins or reefs which intersect metamorphic rocks, and to some extent also in the wall-rock of these veins. Metamorphic rocks which are thus intersected are generally chloritic, talcose, and argillaceous schists; also, though less commonly, mica- and hornblende-schists, gneiss, diorite, and porphyry, and, still more rarely, granite. Gold is frequently found crystalline, the commonest forms being the octohedron and tetrahedron. The crystals are, however, sometimes acicular, through elongation of these two forms, passing into filiform, reticulated, and arborescent shapes and occasionally exhibiting a spongy form from the aggregation of filaments. It frequently occurs in masses termed nuggets, in thin laminæ, and often in flattened grains or scales and in rolled masses in sand or gravel. Sometimes indeed it is so finely disseminated throughout the quartz that it is not visible, though present in quantities sufficient to pay for its extraction.

The occurrence of gold is not confined to the above-named rocks, but it is found in many formations, even up to the chalk.

The sands, gravels, and clays formed by the disintegration of the gold-bearing rocks form one of the most important sources of the precious metal, and these alluvial deposits often occur of considerable thickness and of great extent, those of the Yuba, an affluent of the Feather River in California, varying from 80 to 250 feet in depth and averaging probably 120 feet.

578 Although gold occurs widely distributed in nature it is only in certain places where it is found in quantities sufficient to repay the process of extraction. The most important European localities are Hungary and Transylvania.

[1] Those interested in the processes employed by the alchemists in the search after the philosopher's stone are referred to Thomson's *History of Chemistry*.

These formerly yielded a considerable portion of the gold which came into commerce; but their importance as gold-bearing localities has recently much diminished. Gold is also found in the Alps, but the mines there, which were worked from the times of the ancients, are now altogether abandoned or worked but very slightly. Thus, for instance, at Zell in the Zillerthal in the Tyrol, and at Vöröspatak in Transylvania, gold-mining is still carried on.

The sands of all the rivers which flow from the Alps contain gold. Thus, for instance, the sands of the Upper Rhine have for centuries been washed for gold although the richest portion of the sand contains only about 56 parts of gold to 10 million. Gold has also been found in many streams in Cornwall, and the precious metal has been worked at Dolgelly and other parts of North Wales, in Scotland, especially near Leadhills, and in Glencoich, and other parts of Perthshire, in County Wicklow, and in Sweden. Gold has also been found in Spain, where mines were worked by the Romans. In Asia gold occurs chiefly on the eastern flanks of the Urals and in other parts of Siberia, but this metal has been found in almost all parts of this continent, especially in India. The vessels of gold in the possession of the ancient Scythians, which according to Herodotus were said to have fallen from the skies, were probably made from Uralian gold. The mines in the Urals were however not opened until the year 1819, but they soon became of such importance that they supplied the greater portion of the world's requirements until the discovery of Californian gold.

Africa also contains much gold. Thus a considerable quantity of gold-dust has been found in Abyssinia, also on the coast opposite Madagascar, supposed to be the *Ophir* of Solomon, and in various parts of the interior of the western portion of the continent whence it was formerly shipped to the gold-coast. Indeed this source, together with that of Hungary and the Brazils, yielded the chief supply of gold up to the beginning of the present century.

About that time gold was first found in the United States, and gold-mining was carried on in the Carolinas, as well as in Virginia and Georgia.

579 Since the year 1849 gold-bearing regions have become known which in richness far surpass all those hitherto known. In that year gold was discovered in California by Colonel Sutter, who having erected a saw-mill saw that the water which was to work the mill contained particles of gold. The attempt to keep this discovery secret naturally failed, and the few hundred

inhabitants of the city of San Francisco rushed to the gold-diggings, and these were soon followed by emigrants from all parts of the world. For the first few years Californian gold was obtained entirely from alluvial washings, but since 1852 true gold-mining has been on the increase. The gold-bearing quartz-reefs are often very large. Those on the Mariposa estate average twelve feet, but in some cases extend to 40 feet in breadth.[1] Besides those of California, other considerable gold-fields exist in the western portion of the North American continent, reaching from Mexico up to British Columbia. The enormous extent of some of these mines may be gathered from the following statement. Two neighbouring mines near Virginia City in Nevada yielded in the year 1877 the following quantities:

	Ore in tons.	Value per ton in dollars.	Value in dolls. of the obtained	
			Gold.	Silver.
Californian mine . .	213,683	93	9,386,745	9,538,105
Consolidated Virginian mine . .	143,200	96	6,210,518	7,523,482
	356,883		15,597,263	17,061,587

And these two companies in the same year paid a dividend to the shareholders of 22,680,000 dollars.

580 Australia is another country especially rich in gold-fields. The principal gold-mines occur in the table-lands of New South Wales and along the continuation of the Australian cordillera in Victoria.

It is a matter of general notoriety that many years before anything was published respecting the existence of gold in Australia, gold was often brought into Sydney by shepherds and settlers in the bush. The actual occurrence of gold in Australia was, however, first discovered by Count Strzelecki in the year 1839, but this was not made known at the time, inasmuch as the Governor feared the consequences of such a statement in the then condition of the colony. In 1843–4 Count Strzelecki returned to England and exhibited his nuggets and gold specimens to Sir Roderick Murchison, who, arguing from the comparison of the geological features of these and the gold-bearing Urals, predicted that gold would be found widely distributed in the eastern chains of the Australian mountains. In the years 1841–3 gold was also found by the Rev. W. D. Clarke, an

[1] See J. D. Whitney's *Geology of California*.

Australian geologist. To Mr. Hargreaves, an old Californian gold-digger, however, the honour belongs of proving, in 1851, that gold exists in large quantities in various parts of the colony, and of showing how it could be readily obtained from alluvial deposits by means of the cradle. The first discovery of workable gold-fields was made at Ophir, and this soon led to the finding of the precious metal in the soil and rocks of the colony over tracks many miles in extent. After a short time the proclaimed gold-fields extended, with a few intervals, the whole length of the colony, and westward about 200 miles, comprising an area of about 1,356 square miles, and numbering more than eighty distinct fields.[1]

The following table gives the weight and value of the gold produced in New South Wales each year from 1851 to 1874:

Quantity of Gold produced in New South Wales.

Year.	Oz.	Value.		
		£	*s.*	*d.*
1851	144,120·808	468,366	0	0
1852	818,751·93	2,660,946	0	0
1853	548,052·99	1,781,172	0	0
1854	237,910·69	773,209	0	0
1855	171,367	654,594	0	0
1856	184,600	689,174	0	0
1857	175,949	674,477	0	0
1858	286,798·65	1,104,174	12	2
1859	329,363·41	1,259,127	7	10
1860	384,053·91	1,465,372	19	9
1861	465,685·37	1,806,171	10	8
1862	640,622·79	2,467,779	16	1
1863	466,111·63	1,796,170	4	0
1864	340,267·02	1,304,926	7	11
1865	320,316·73	1,231,242	17	7
1866	290,014·21	1,116,403	14	5
1867	271,886·47	1,053,578	2	11
1868	255,622·38	994,655	0	5
1869	251,491·79	974,148	13	4
1870	240,858·10	931,016	8	6
1871	323,609·79	1,250,484	15	11
1872	425,129·91	1,643,581	16	11
1873	361,784·71	1,395,175	8	7
1874	270,823·31	1,040,328	13	6
Total	8,205,232·598	£30,536,246	10	6

[1] Liversidge, *Trans. Roy. Soc. N.S.W.* ix. 153.

The quantity and value of gold yearly exported from Victoria from 1851 to 1865, is given below.

Quantity of Gold exported from Victoria.

Year.	Quantity.			Value.		
	Oz.	dwt.	gr.	£	*s.*	*d.*
1851	145,137	3	12	580,548	12	0
1852	1,988,526	10	13	7,954,106	0	0
1853	2,497,723	15	16	9,990,895	0	0
1854	2,144,699	9	19	8,578,797	16	0
1855	2,575,745	4	17	10,302,980	16	0
1856	2,985,695	17	0	11,942,783	8	0
1857	2,761,528	8	0	11,046,113	12	0
1858	2,555,263	0	0	10,221,052	0	0
1859	2,280,525	14	0	9,122,102	16	0
1860	2,128,466	11	0	8,513,866	4	0
1861	1,978,864	13	0	7,915,458	12	0
1862	1,662,448	18	0	6,649,795	12	0
1863	1,627,066	0	0	6,508,264	0	0
1864	1,545,449	15	0	6,181,799	0	0
1865	1,545,450	0	0	6,181,800	0	0
Total	Oz. 30,422,591	0	5	£121,690,363	8	0

In addition to the above, which was exported through the Custom House, it is estimated that about 3,941,150 oz. was also sent away through other channels, or manufactured.

The amount of Victorian gold, alluvial and quartz, raised since 1868 is found in the following table:

Year.	Alluvial.	Quartz.
	Oz.	Oz.
1868	1,087,502	597,416
1869	934,082	610,674
1870	718,729	585,575
1871	698,190	670,725
1872	639,551	691,826
1873	504,250	666,147
1874	433,283	664,360
1875	426,611	641,806
1876	357,901	605,859
1877	289,754	519,899

These figures show a steady annual decrease since 1868 in the amount of gold obtained from alluvial deposits; the total decrease is 797,748 oz. This reduction in the yield is owing to the gradual and inevitable exhaustion of the auriferous drifts of the earlier discovered gold-fields, and to the non-discovery in later years of mining areas of sufficient extent and richness to compensate for the diminished yields obtained from the older alluvial workings. The yield of gold from quartz-mines has not increased during 1877, and the return for this year is the smallest recorded during the past ten years.[1]

Gold has also been found in New Zealand, Queensland, Tasmania, New Caledonia, and also in India. The Australian is, as a rule, much purer than the Californian gold, but it is a singular fact that the average fineness of the gold found in the several Australian colonies shows a regular depreciation as we advance northwards. Thus the average fineness of Victorian gold is about 960; that of the New South Wales gold is 935, while still further north in Queensland the average fineness is 872, and Maryborough gold contains only 85 per cent. of gold and as much as 14 per cent of silver.[2] Very large nuggets occur in Australian fields; thus, for instance, one found at Ballarat weighed 184 pounds and was valued at 8,376*l.* 10*s.* 6*d.*

Composition of Native Gold. The following table gives the composition of several kinds of native gold:

Locality .	Barbara (Siebenbürgen).	Katharinenberg (Ural).	Senegal.	Bolivia.	California.	Australia.	Mitta-Mitta (Australia)
Analyst . .	Rose.	Rose.	Levol.	Forbes.	Hunt.	Northcote.	Ward.
Gold . .	84·80	93·34	94 40	94·73	89·24	99·28	89·57
Silver . .	14·68	6·28	5·85	5·23	10·76	0·44	10·43
Iron . .	0·13	0·32	—	0·04	—	0·20	—
Copper .	0·04	0·06	—	—	—	0·07	—
Platinum.	—	—	0·15	—	—	—	—
Bismuth .	—	—	—	—	—	0·01	—
	99·65	99·90	100 00	100 00	100·00	100·00	100·00

581 *Gold-mining.* The first method of gold-mining, namely, *alluvial-washing* or *placer-digging*, as it is termed in California, carried on from the simple pan-washing to hydraulic-mining on a stupendous scale, necessarily requires a considerable quantity

[1] *Mineral Statistics of Victoria for* 1877. (Published by the Minister of Mines.)
[2] F. B. Miller, *Trans. Roy. Soc. N.S. W.* 1870.

of running water. This or a similar process was in use amongst the ancients; thus Pliny describes the "bringing of rivers from the mountains, in many instances for a hundred miles for washing the débris," &c., &c.

The washing apparatus is simple enough though frequently ingenious. The simplest of all these operations is that termed *pan-washing*, in which a shallow pan is used, of iron or zinc, sinking into a cavity in the middle into which the heavy particles collect, whilst the lighter dirt is washed away. The wash-dirt or wash-stuff is brought into the pan in a stream of running water and the mass well stirred up with the hand so that the larger stones and heavy particles are left whilst the mud flows over the edge of the pan. The gold, which is found when the stones are picked out, is usually mixed with magnetic sand; it is dried and then brought into a shallow dish and the black sand separated by blowing, the whole being kept in a state of constant rotation.

The *cradle* is another simple apparatus for gold-washing, much used in the early days of the gold discoveries in California and Australia. It consists of a trough or cradle of wood or iron six or seven feet in length under which rockers are placed, so arranged that the cradle has a slanting position to allow the mud and water to run off. At the top of the cradle is a grating or sieve upon which the wash-stuff is thrown, and tranverse bars of wood are placed across the bottom of the cradle to arrest the passage of the heavier particles of gold. Four men are needed to work this efficiently; one digs out the auriferous wash-stuff, another brings it to the cradle, a third rocks the trough, and the fourth attends to the proper supply of water and the uniform washing of the material.

582 *Hydraulic Gold-mining.* The system of hydraulic mining carried out in California on a stupendous scale will best be understood by the following quotation from Professor Silliman :—

As the shallow placers in the ravines and river-beds in California became exhausted, the necessity for adopting a method for economically working the deep placers was felt. This has been done by the introduction of hydraulic mining, requiring the construction of canals and aqueducts to convey water from the fountain-heads to the ground to be worked, as well as the opening of tunnels and shafts in the bed-rock, in which the gold occurs, for the discharge of the gravel. The capital and labour expended on these works in California since the year 1853 has

been enormous. In order to work the process satisfactorily the whole mass of the auriferous gravel must first be moved quite down to the bed-rock. This must be accomplished by water alone, and the whole compact conglomerate must be thus mechanically disintegrated whilst the gold is deposited and collected in the process of washing. These conditions are in practice met by the following arrangement. The mining ground having been selected, a tunnel is projected from the nearest and most convenient ravine. So that starting in the bed-rock on the face of the ravine it shall approach the centre of the gravel mass to be moved at a gradient of from 1 in 12 to 1 in 20. This tunnel is usually six feet wide and seven feet high and varies in length from a few hundred feet to many thousands. The end of the tunnel is arranged so as to be from 50 to 100 or more feet below the under surface of the gravel. At this point a shaft is sunk through the gravel and bed-rock until it intersects the tunnel. Throughout the length of the tunnel sluice-boxes are laid so as at once to direct the stream of water and to save the gold. For this purpose a trough of strong planks is built in the tunnel 2½ feet wide, the bottom of which consists of blocks of wood placed about two inches apart, and in the interstices thus left a small quantity of quicksilver is placed to aid in catching the heavy particles of gold which fall into these hollow places. The water from the canal is brought by aqueducts to the head of the mining-ground with an elevation of 100 to 400 feet above the bed-rock and it is conveyed into the bottom of the mining claims by iron pipes sustained on timbers. These communicate at the bottom with a strong box of cast-iron, at the top and sides of which are openings for the adaptation of flexible pipes which end in nozzles sometimes of three to five inches in diameter, from which a stream of water issues under great pressure and with immense force, and these are allowed to play, as is seen in Fig. 168, on the surface of the auriferous conglomerate. Under the continuous action of this enormous mechanical force aided by the softening power of water, large sections of the mass come crushing down with great violence; the débris, quickly disintegrating and disappearing under the resistless force of the torrent of water, is hurried forward to the mouth of the shaft down which it is precipitated with the whole volume of turbid water. This then finds its way down the tunnel which is cleared at intervals of from ten to twenty days, the whole of the pavement of the blocks

being removed and the amalgam of gold and "rich dirt" contained in the interstices is taken out, the blocks replaced, and the operation continued. Rude as this method of saving the gold appears, experience shows that more gold is saved by it than by any other method of washing yet devised, while the economical advantages it offers are incomparably greater than any other. Indeed it would be absolutely impossible to handle so vast a body of poor material in any other way now known. To show the enormous advantage gained by the present system

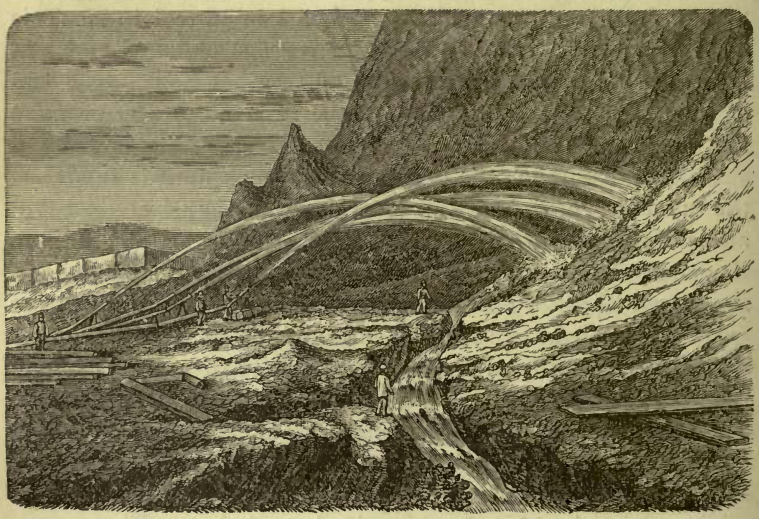

Fig. 168.

of working compared with those formerly in use, Mr. Black, a Californian engineer, states that taking a miner's wages at four dollars a day, the cost of handling a cubic yard of auriferous gravel is as follows:

With the pan	20 dollars.
„ „ rocker . . .	5 „
„ „ long tom . . .	1 dollar.
„ „ hydraulic process	0·2 „[1]

583 *Quartz-mining.* The mining operations carried on in the gold-bearing quartz-reefs are not different from those used in the case of other ores. In order to extract the gold from the

[1] B. Silliman, "On the Deep Placers of the South and Middle Yuba, California," *Amer. Journ. Sci. and Art*, [2], xl. 1.

gangue the whole mass must be well pulverized. A variety of mechanical contrivances are employed for this purpose, stamping with iron stamps being probably the best. The gold is extracted from the powdered mineral by means of mercury, to which sometimes a small quantity of sodium is added. The application of sodium was proposed by H. Wurtz of New York, and by Mr. Crookes in England, and for some time it was employed considerably, but its use has not become general. The use of sodium was said to be especially advantageous in the case of the presence of pyrites. After the gold amalgam has been well pressed, it is heated in iron retorts, and the porous gold which remains melted and cast in iron moulds.

584 *Gold Extraction by Chlorine.* For the purpose of extracting gold from auriferous pyrites Plattner's chlorine method is sometimes employed. In California the "tailings" and deposited auriferous pyrites are roasted in order to remove the sulphur and arsenic, then moistened with water, and placed in tubs furnished with false bottoms, beneath which chlorine is introduced. After all the air has been replaced by chlorine, and the whole mass has become impregnated with this gas, the tubs are allowed to stand for about twelve hours. After the lapse of this time the soluble gold chloride is washed out with water, the metal precipitated from solution by the addition of green vitriol, and the powdered gold dried and fused with borax.

Rivot's Process. The extraction of gold from auriferous arsenical pyrites by means of mercury is a somewhat difficult operation, as the amalgamation of the gold does not take place satisfactorily. Indeed, in Australia the problem of extracting gold from this source has not yet been satisfactorily solved, and a large proportion of the gold occurring under these circumstances is now lost.[1] In California a process known as Rivot's has been employed with good results, one peculiarity of which consists in roasting the ore with superheated steam previous to amalgamation.

585 *Parting by Sulphuric Acid.* It has already been stated that native gold always contains more or less silver, and in the same way silver is frequently auriferous. Nitric acid was formerly used for the purpose of separating these two metals, being first employed, it would appear, at Venice in the fifteenth century, for extracting the gold from Spanish silver. This method

[1] Dixon, "On a Method of Extracting Gold, Silver, and other Metals from Pyrites," *Proc. Roy. Soc. N.S. W.* 1877, 93.

remained in general use up to the beginning of this century, notwithstanding Scheele's discovery in 1753 that sulphuric acid could be employed for this purpose. In a memoir on the subject, read before the Stockholm Academy, he says: "Sulphuric acid also dissolves silver when no water is amongst it, but gold is not in the least degree altered, so that silver and gold can be thus completely separated from one another; but such an oil of vitriol is much dearer than nitric acid, and for this reason it is not advisable to use it for this purpose, as there are other acids which cost less." Hence it was only when sulphuric acid became cheaper that the process of separation by its means could be carried out, and this was done by Darcet in 1802.

In order to separate the two metals by this method the alloy must not contain more than 25 per cent. of gold. If it be richer than this, it must be first melted with the necessary quantity of silver. The granulated alloy is heated in cast-iron boilers, together with two and a half times its weight of concentrated sulphuric acid of specific gravity 1·84. Each vessel is covered with a dome of lead, and the sulphur dioxide which is evolved during the solution of the silver is either allowed to escape into the air or led into sulphuric acid chambers. As soon as no further evolution of this gas takes place, sulphuric acid, of specific gravity 1·69, is added for the purpose of dissolving the copper vitriol. The clear liquid is then allowed to flow into leaden pans containing the mother-liquors of copper vitriol formed in the next operation, and the whole is heated by steam in order to keep the slightly soluble silver sulphate in solution. Here a further quantity of gold is deposited, the clear liquid is again drawn off, and the silver precipitated by means of metallic copper. The finely-divided gold is again treated with sulphuric acid in a platinum vessel in order to render it completely free from silver, and after having been well boiled, it is washed and fused in a black-lead crucible with bicarbonate of soda.

An improvement in this process, recommended by Rössler,[1] consists in allowing the sulphuric acid solution of silver to crystallize, with addition of a small quantity of water. The yellow crystals of silver sulphate are then mixed with water, and metallic iron gradually added, so that all the silver is precipitated, but the whole of the copper remains in solution. The

[1] *Lieb, Ann.* clxxx. 240.

impurities introduced by the iron are removed in the slag on fusion, and the silver is purer than when the copper is thrown down with it.

586 *Refining of Gold.* The gold employed for coinage, when it does not contain more than 10 per cent. of silver, is now usually purified by Mr. F. B. Miller's process with chlorine gas, first introduced by him in the Sydney Mint and now adopted in the Royal Mint by Mr. Chandler Roberts. This process consists in melting the gold in a clay crucible which has been glazed inside with borax, and passing chlorine gas through the molten metal by means of a clay pipe. The chlorine at once combines with the silver to form silver chloride, which rises to the surface of the molten metal, whilst the chlorides of zinc, bismuth, antimony, and arsenic, should these metals be present, are volatilised and the pure gold remains beneath. A layer of melted borax is placed on the top of the fused mass in order to prevent the silver chloride which is formed from being volatilised. The fineness of the gold thus prepared varies from 991 to 997 in 1,000 parts, whilst the metal obtained by other refining processes frequently contains a larger quantity of silver, unless indeed it has been worked up by the method already described as Rössler's, when it appears to be chemically pure.

In order to prepare gold absolutely free from silver, the metal is dissolved in aqua-regia, the solution concentrated in order to drive off the nitric acid, and diluted with water, the solution filtered, and the metallic gold precipitated by a reducing agent. For this purpose ferrous sulphate is usually employed, the following reaction taking place:

$$2AuCl_3 + 6FeSO_4 = 2Au + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

When the gold solution is poured into that of the iron-vitriol the gold is obtained in a very finely-divided state. If the solutions be mixed in the reverse order, the precipitated gold is scaly and more lustrous. Gold may also be precipitated by sulphur dioxide, by a hydrochloric acid solution of arsenic trioxide, antimony trioxide, or other reducing agents, as well as by mercurous nitrate, oxalic acid, &c. If a small quantity of oxalic acid and an excess of potassium carbonate be added to a solution of gold, a clear solution is obtained which is decomposed on the addition of more oxalic acid, and this, when quickly heated to boiling, yields precipitated gold in the form of a fine yellow

spongy mass. In order to obtain the gold in the coherent state, it is fused with the addition of borax and nitre.

587 *Properties.* Gold is distinguished from all the other metallic elements by its bright yellow colour. It crystallizes in the regular system, and in the native state is often found in distinct though small crystals. Some Australian gold worth about £1,100 consisted of grains from the size of a large pea to that of small grains of sand, all of which were more or less perfect dodecahedrons.[1] Native gold has also been found crystallized in a very great variety of other forms of the regular system.[2] These small crystals are frequently connected together, so as to form hair-like filaments, termed *moss-gold.* Liversidge[3] has obtained this form of gold artificially. He noticed the occurrence of crystallized gold in certain specimens of Australian auriferous pyrites, and he therefore roasted this mineral in a muffle, for the purpose of removing arsenic and sulphur, but at a temperature insufficient to bring about the fusion either of the mineral or of the gold. On removing the sample from the muffle, small cauliflower-like excrescences of metallic gold were observed on the surface of the mass, these excrescences being composed of fine filaments of the metal often wound round in spiral coils.

Gold precipitated from a concentrated solution by ferrous sulphate forms very small cubes, and that obtained by reduction with oxalic acid consists of minute octohedrons, which are usually much distorted. When an amalgam containing 5 per cent. of gold is heated for eight days to 80°, and then treated with hot nitric acid, an aggregate of crystals, some of which are 6 mm. in length, may be obtained. These, after heating to get rid of the mercury, have a bright lustrous appearance.

Gold is softer than silver, and is the most ductile of metals. This was known to Pliny, who says: "Superque omnia netur, ac texitur lanæ modo."[4]

Although the relation which the Roman weights and measures bear to those in use in the present day is still somewhat uncertain, the following statement may be of interest as showing the progress of the art of gold-beating. In the first place we read in Pliny, "nec aliud laxius dilatatur, aut numerosius dividitur, ut pote cujus unciæ in septingenas et quinquagenas,

[1] Dana, *System of Mineralogy*, 5 Ed. p. 8.
[2] G. von Rath, *Zeitsch. Krystall. Mineralog.* i. 1.
[3] *Proc. Roy. Soc. N.S. Wales*, 1876, 125.
[4] *N.H.* xxxiii. 19.

pluresque bratteas, quaternum utroque digitorum spargantur."[1] Then in 1621 Mersenne mentions that the Paris gold-beaters were in the habit of obtaining 1,600 leaves from one ounce of gold, which would cover 105 square feet. In 1680 Halley states that in his time a grain of gold could be drawn into a wire 98 ells in length, whilst Reaumur mentions in 1711 that one ounce of gold can be hammered out so as to cover 146½ square feet, and according to newer statements one grain may be made to cover 56·75 square inches, or one ounce to cover 189 square feet, whilst 280,000 leaves have to be placed one upon another to occupy the thickness of one inch. One grain of gold also serves to gild two miles of fine silver wire, whilst the thickness of such deposits of gold as, for example, that on gold lace is about 0·000002 mm. Gold is extremely ductile, and gold wire can be drawn so fine that 3,240 meters weigh only one gram. Gold-leaf has usually a thickness of about 0·0001 mm., and allows green light to pass through. Metallic gold can be precipitated in a dilute liquid in so fine a state of division that it remains suspended, and under these circumstances it appears by reflected light, of a purple-red, whilst by transmitted light it assumes a blue colour.

The relations of finely-divided gold to light have been carefully examined by Faraday.[2] By spreading a leaf of gold on a glass-plate and then pouring on to it a solution of potassium cyanide, Faraday succeeded in obtaining films of gold of extreme tenuity. The green colour which ordinary gold-leaf exhibits by transmitted light passes into a ruby-red when the highly attenuated film is heated to 316°. The red colour of ruby glass is due to the presence of metallic gold in an extreme state of division. This is also the case with the above-mentioned film, the original green tint of which can be brought back by burnishing its surface.

At 13° gold has a specific gravity of 19·265 (Matthiessen); it fuses according to Pouillet at 1381°, and according to Becquerel[3] at 1037°, expanding considerably in the act of fusion, and forming a bluish-green liquid. It volatilizes at a very high temperature, as when auriferous platinum is fused in the oxy-hydrogen blowpipe, or when a powerful electric discharge is passed through a thin gold wire.

[1] *N.H.* xxxiii. 19. An ounce of gold can be hammered into 750 leaves, each of which is 4 digits (about 3 inches) square.

[2] *Phil. Trans.* 1857, p. 145.

[3] *Compt. Rend.* lvii. 855.

Gold is not attacked at any temperature either by oxygen or by water, and it also remains unacted upon when fused with chlorate of potash. Alkalis and the nitrates, however, attack it. Gold does not dissolve in any simple acid, with the exception of selenic (Mitscherlich), but it dissolves readily in aqua-regia, or in any other acid liquid in which chlorine is evolved.

588 *Purple of Cassius.* This body, of which mention has already been made as being used in the preparation of ruby glass, was discovered by Andreas Cassius, who, however, did not publish anything on the subject, though his son of the same name published a pamphlet in 1685 entitled, *De extremo illo et perfectissimo naturæ opificio ac principe terrenorum sidere, Auro, et admiranda ejus natura—cogitata, experimentis illustrata.* In the previous year however, a Hessian mining official, Orschal, published a paper, *Sol Sine Vesta: or, Thirty Experiments to Draw out its Purple from Gold.* He describes that he had learned the process from Cassius, and that it consisted in precipitating gold with tin. After that time many investigations were made on this pigment without any satisfactory explanation of its chemical nature being arrived at. A variety of receipts were given for its preparation, in all of which gold chloride was precipitated by a mixture of stannous and stannic chlorides. This precipitate is, according to the mode of preparation, either of a dark purple-red, or of a reddish-brown colour, both yielding a brown powder on drying. The process by which the finest purple is obtained is, according to Fuchs, to add stannous chloride to a solution of ferric chloride until the yellow colour is changed to a pale green, and then to precipitate the gold solution with this mixture. The precipitate contains tin oxide in varying quantities, and some chemists have supposed that the compound is a gold stannate, but this view is contradicted by the fact that when purple of Cassius is dried and then triturated, the powder assumes a metallic lustre, and on heating does not evolve oxygen. For this reason others have regarded the substance as a mixture of tin oxide and very finely-divided gold. The fact, however, that the freshly precipitated and moist pigment is soluble in ammonia tells against this latter supposition, as does the action of light on the liquid, for gold is then precipitated, whilst ammonium stannate remains in solution. The literature respecting the purple of Cassius has been collected by J. C. Fischer.[1]

589 *Gilding.* The art of gilding is mentioned by Moses, and

[1] *Dingl. Polyt. Journ.* clxxxii. 39.

Pliny states that objects of wood and marble are gilt by means of gold-leaf, whilst metallic surfaces are gilt by help of quick-silver. Gold-leaf is obtained from gold-foil by hammering pieces, each having an area of a square inch and weighing six grains, first between sheets of vellum or tough paper, and afterwards between leaves of gold-beater's skin—a material prepared from the cæcum of the ox. The small cuttings and waste leaf are employed for the preparation of the shell gold used by painters.

A variety of methods are employed for gilding metals. In gilding by immersion the well-cleaned objects are dipped into a boiling solution of gold chloride and bicarbonate of potash; whilst in wash-gilding a gold amalgam is rubbed on the surface, the mercury afterwards driven off by heating, and the surface either burnished, or deadened by heating it with a fused mixture of common salt, saltpetre, and lime, when a small quantity of chlorine is liberated which etches the gold. These older methods have now, however, been almost completely supplanted by the *electro-deposition of gold.* For this purpose a solution of gold chloride and potassium cyanide is employed, a gold plate being used as the positive electrode. The colour of the deposited gold can be modified by adding to the gold solution salts of silver or copper, as well as both of these, when alloys are deposited.

590 *Alloys of Gold.* Pure gold is very soft, and is soon worn away by use. Hence, for the purpose of coinage, and for the use of the goldsmith, it is alloyed with copper or silver, or with both together, the resulting alloys being much harder than pure gold. Copper imparts to the gold a red colour, and lowers its fusing-point. This alloy was formerly called red-carat gold, because the fineness of a gold alloy used to be universally expressed in carats, 24-carat gold being pure gold. In England at the present time five legal standards exist for gold-ware; 22-carat, or standard gold, 18, 15, 12, and 9-carat gold, the meaning of this being that 24 parts by weight of the alloy contain 22, 18, 15, 12, and 9 parts of gold respectively.

In the case of the coinage, however, the fineness of gold is generally expressed in parts per 1,000. Thus, for instance, English standard gold, being a 22-carat gold, has a fineness of 916·66. In the German, American, and Italian coinage standard gold is of 21·6 carats, or has a fineness of 900. Red-carat ornaments are frequently covered with a thin coating of

pure gold by heating them and dipping them for a short time in dilute nitric acid.

The alloys of gold and silver are called white alloys, and have a greenish-yellow colour if they do not contain too small a quantity of silver, whilst when the latter metal is present in larger amount the alloy assumes a yellowish-white shade. A gold-silver alloy occurs naturally as electrum, often found in crystals belonging to the regular system.

Trinket gold contains both copper and silver. It is hard, and, according to the proportion of its materials, possesses either a yellowish-red or a whitish colour.

Gold-Amalgam. Gold readily combines with mercury. An amalgam containing 2 atoms of gold to from 3 to 16 atoms of mercury,[1] crystallizes in four-sided prisms. An amalgam which occurs in California has the composition Au_2Hg_3, and another, $(AuAg)_2Hg_5$, is found in the form of white grains, together with platinum, in Columbia.

GOLD AND OXYGEN.

591 These elements combine in two proportions:

Gold Monoxide or Aurous Oxide, Au_2O.
Gold Trioxide, or Auric Oxide, Au_2O_3.

Gold Monoxide, Au_2O, is obtained by decomposing the corresponding chloride, AuCl, with cold dilute caustic potash (Berzelius). Another method of preparation is to boil a solution of gold trichloride with the potassium salt of acetic, tartaric, or other organic acid.[2] It is a powder which, when moist, has a violet-black, and when dry assumes a violet-brown tint, and is decomposed at 250° into gold and oxygen. It decomposes on contact with hydrochloric acid, slowly in the cold and quickly on boiling, into gold and the trichloride. Sulphuric acid and nitric acid do not act upon it, but it is easily dissolved by aqua-regia. Although unacted upon by acids, it is at once decomposed by weak bases.

Of its salts, the chloride and iodide, and a few others, form peculiar double salts with the salts of the alkali metals.

[1] Figuier, *Ann. Chim. Phys.* [3], xi. 336.
[2] See vol. ii. part. i. p. 10.

592 *Gold Trioxide*, Au_2O_3. The substance, termed calx of gold by the early chemists, was nothing more than the finely-divided metal. Bergmann was the first to state that the precipitate produced by alkalis in the gold solution is dephlogisticated gold; but the oxide was examined more carefully in 1806 by Proust, and in 1811 by Oberkampf. Gold trioxide is a blackish-brown powder, obtained by heating the hydroxide to 100°. If this be more strongly heated, it gives off oxygen, and is converted into a brown powder of metallic gold.

Gold Trihydroxide, $Au(OH)_3$, is best obtained by heating a solution of gold trichloride with an excess of magnesia, and well washing the precipitate with nitric acid (Pelletier). The gold solution may also be treated with caustic potash until the precipitate which is formed is redissolved, and then the dark-brown solution boiled until it becomes of a light-yellow colour, a slight excess of sulphuric acid added, and the precipitate washed. The hydroxide thus prepared always contains a little potash, and for this reason it is dissolved in concentrated nitric acid, again precipitated by water, and dried in a vacuum. According to Thomsen it is best prepared by warming a dilute solution of gold trichloride with caustic potash, and precipitating the brown solution by Glauber-salt, when it is obtained in a form resembling precipitated ferric hydroxide. In the moist state it varies in its appearance according to the mode of preparation, being a yellow, olive-green, or brown powder, which on drying becomes brownish-black, and decomposes on exposure to light with evolution of oxygen. When warmed with alcoholic potash the metal is reduced in the form of fine glistening scales, which are employed in miniature painting. It is a weak base, which dissolves slightly in concentrated sulphuric acid, and more readily in nitric acid, from which solutions it is again precipitated on the addition of water. It forms the corresponding haloid salts with hydrochloric and hydrobromic acids. Gold trioxide is an acid-forming oxide, and its salts are termed aurates.

If gold be treated with a quantity of aqua-regia insufficient to dissolve the whole, and containing an excess of hydrochloric acid, and if a sufficient quantity of bicarbonate of potash be then added to the acid liquid so as to redissolve the precipitate which is first formed, an olive-green precipitate is thrown down on warming. This, when dried in the air, becomes black, and possesses the composition Au_2O_2. If on the other hand the

gold solution contain an excess of nitric acid, an orange-red precipitate having the composition Au_2O_4 separates out.[1]

593 *Ammoniacal Auric Oxide*, or *Fulminating Gold*, $Au_2O_3(NH_3)_4$. The preparation of this compound was first described with great accuracy by Basil Valentine in his *Last Testament*. He obtained it by dissolving gold in *aqua-regia* mixed with *salarmoniac*, precipitating with *sal-tartari* (potashes), and subsequently washing with water. He then says: "Dry the gold-calx in the air where no sun shines, and especially not over the fire, for as soon as this powder is exposed to a little warmth it ignites and does a greal deal of damage, for it then explodes with such great power and might that no man can withstand." He then describes its properties, and, amongst others, that it loses its explosive power when heated with sulphur. The name of fulminating gold (aurum fulminans) was given to it by Beguin in 1608. It was, however, also known under other names, and was used as a medicine. Angelus Sala, writing in the first half of the seventeenth century, mentions that no fulminating gold can be prepared if aqua-regia made with hydrochloric acid be employed instead of that made with sal-ammoniac, and Glauber says that the preparation obtained by means of volatile alkali (carbonate of ammonia) fulminates much more strongly than that made with *oleum tartari* (carbonate of potash). In spite of these observations but few chemists believed that the volatile alkali took part in the composition of the substance, and a great number of erroneous observations have been made on the subject of the composition of fulminating gold.[2] Even Black in 1756 stated that the explosion was due to the sudden evolution of fixed air, although Kunkel, a very accurate observer, had already pointed out the true cause. For in his *Laboratorium Chymicum*, which appeared in 1716, fourteen years after his death, he describes the preparation of fulminating gold, and discusses the various reactions which take place. He then continues: "Once I precipitated the gold with *oleum tartari*, distilled the menstruum to dryness, and then edulcorated; and I thus obtained a fine gold calx which became brown but did not fulminate at all; when, however, the same substance was imbibed several times with *spiritus urinæ* and very gently dried, it exploded violently." He also says that when this substance is imbibed and afterwards distilled with oil of vitriol, an acid sal-volatile sublimes in the

[1] Prat. *Compt. Rend.*, lxxx. 845.
[2] Kopp, *Geschichte der Chimie*, iv. 210.

neck of the retort. "Hence," he adds, "thou canst see whence the power in the *aurum fulminans* comes, namely from the *sal-volatile concentratum*." This view was confirmed by the experiments of Bergmann and Scheele, who considered fulminating gold to be a compound of ammonia and gold calx. Hence the Lavoisierians termed this compound *oxyde d'or ammoniacal*. The composition of this body was subsequently more exactly investigated by Dumas.[1]

Fulminating gold is best obtained by the action of ammonia on gold hydroxide, or by precipitating gold chloride with ammonia or its carbonate. It is a green or brown powder, which explodes most violently when in the dry state either on percussion or when heated. The violence of the detonation is increased by washing with hot water, and when the compound is prepared by precipitation from the chloride it is usual to add some alkali in order to remove the whole of the chloride. The explosion can be brought about by rubbing on paper, and when it is warmed for a short time to 100° it becomes so unstable that it can scarcely be touched without undergoing decomposition.[2]

AUROUS SALTS.

594 *Aurous Chloride*, or *Gold Monochloride*, AuCl, is best obtained by carefully heating the trichloride to 185°. It is a yellowish powder, which readily decomposes into gold and the trichloride.

Aurous Bromide, AuBr, is formed as a greenish-yellow micaceous powder when brom-auric acid, $AuBr_4H$, is heated to 115°. It is insoluble in water, and hydrobromic acid decomposes it into gold and the compound from which it has been obtained.

Aurous Iodide, AuI, is formed when hydriodic acid acts upon gold oxide:

$$Au_2O_3 + 6HI = 2AuI + 3H_2O + 2I_2.$$

It is also formed when the trichloride is precipitated by a solution of the iodide. When finely-divided gold is boiled with hydriodic acid and a small quantity of nitric acid, and the filtrate allowed to run into hydriodic acid, a lemon-yellow

[1] *Ann. Chim. Phys.* xliv. 167.
[2] J. Thomsen, *Journ. pr. Chem.* [2], xiii. 337.

coloured crystalline powder of aurous iodide is formed. It is a very unstable body, which assumes a green colour when exposed to the air and deposits a bright surface of metallic gold on the inside of the vessel in which it stands. The decomposition takes place more quickly on warming, and at 120° it decomposes completely. Aqueous acid decomposes it only when heated.

595 *Sodium Auro-sulphite*, $3Na_2SO_3 + Au_2SO_3 + 3H_2O$, is formed when acid sodium sulphite is added to a boiling alkaline solution of sodium aurate, or when this solution is saturated with sulphur dioxide at 50°. In order to purify it, the sulphurous and sulphuric acids are first precipitated by the careful addition of barium chloride, and then the barium salt corresponding to the above sodium compound is obtained as a purple-red precipitate, which must be quickly washed in absence of air. The moist precipitate is then decomposed by the minimum quantity of sodium carbonate, and any barium salt which may be present precipitated by a small quantity of alcohol, and then, by further addition of the same precipitant the sodium compound is thrown down as an orange-red precipitate. It is very easily oxidizable, but in presence of free sulphur dioxide the solution may be heated to boiling without decomposition occurring. When this solution is precipitated by alcohol the salt is obtained as a purple powder, which appears yellow or green by reflected light.

Ammonium Aur-ammonium Sulphite, $(NH_4)_2SO_3 + 3(NH_3Au)_2SO_3 + 3H_2O$, is obtained by dropping a neutral chloride of gold solution into a warm solution of ammonium sulphite in concentrated ammonia. It forms flat six-sided silky glistening white tablets, and if its solution be acidified, gold separates out. The mother-liquor of the salt contains ammonium auro-sulphite, which can be obtained in a similar way to the sodium salt which it resembles.

Sodium Auro-thiosulphate, $3Na_2S_2O_3 + Au_2S_2O_3 + 4H_2O$, is formed by the gradual addition of a neutral 2 per cent. gold solution to a solution containing three times as much sodium thiosulphate. It is necessary to wait after each addition until the red liquid which is formed becomes colourless. It is then precipitated with strong alcohol, and any common salt and sodium tetrathionate which may be present removed by repeated solution in water and precipitation with alcohol. The salt is formed according to the equation:

$$8Na_2S_2O_3 + 2AuCl_3 = 3Na_2S_2O_3 + Au_2S_2O_3 + 2Na_2S_4O_6 + 6NaCl.$$

It crystallizes in colourless needles, which have a sweet taste. Its solution is not reduced by ferrous sulphate or oxalic acid, nor is it decomposed by hydrochloric acid, or by dilute sulphuric acid. When barium chloride, and afterwards alcohol, are added to its solution a precipitate of the corresponding barium salt is obtained, from which a solution of the acid auro-thiosulphate, $3H_2S_2O_3 + Au_2S_2O_3$, is obtained by addition of the requisite quantity of sulphuric acid. This salt is not known in the anhydrous state, but the solution can be evaporated in the air to a syrupy consistency.

The above compounds do not exhibit the reactions either of the aurous salts or of the thiosulphates, and hence it is assumed that they contain a compound radical, whose hydrogen salt is the last-named compound. They may, therefore, be written as follows:

$$H_3S_4O_6Au.$$
$$Na_3S_4O_6Au + 2H_2O.$$

596 *Aurous Cyanide*, AuCN. This compound is obtained by the addition of hydrochloric acid to a solution of the potassium double salt and evaporation in a water-bath, the residue being washed in the dark. It is a fine yellow powder, showing iridescent colours, which consists of microscopic hexagonal tables insoluble in water, and in the dry state unalterable in the air. It is not attacked by the single acids, but dissolves readily in aqua-regia, as well as in ammonia, sulphide of ammonium, and sodium thiosulphate.

Potassium Auro-cyanide, $KAu(CN)_2$. This compound, largely used in electro-gilding, is best obtained as follows: 7 parts of gold are dissolved in aqua-regia, precipitated by ammonia, the fulminating gold well washed and brought into a boiling solution of 6 parts of pure potassium cyanide. The solution is then filtered and allowed to cool, when, if it is not too dilute, the salt separates out in colourless rhombic pyramids having a pearly lustre. These have a saline and at the same time metallic taste, and are soluble in 7 parts of cold, and in rather less than half their weight of boiling-water. The mother-liquor of these salts contains as impurity potassium chloride and potassium carbonate, and yields on evaporation impure crystals. These are, therefore, decomposed with hydrochloric acid as above described, and the resulting auro-cyanide dissolved in potassium cyanide.

Potassium auro-cyanide is also formed when finely-divided gold is boiled in the presence of air with a solution of potassium cyanide[1]:

$$2Au + 4KCN + O + H_2O = 2AuK(CN)_2 + 2KOH.$$

Ammonium Auro-cyanide, $NH_4Au(CN)_2$, is obtained by mixing a solution of the foregoing salt with one of ammonium sulphate, and removing the potassium sulphate by precipitation with alcohol. The crystals have a disagreeable metallic taste, and are easily soluble in water, alcohol, and ether.

Aurous Thiocyanate is only known in combination with other thiocyanates. The *potassium auro-thiocyanate,* AuSCN + KSCN, is obtained with evolution of thiocyanic acid, when a neutral gold solution is poured into a hot solution of potassium thiocyanate. It crystallizes in yellow obtuse prisms. When hydrochloric acid is added to the solution copper-red needles separate out, and silver nitrate precipitates the double-salt silver-gold thiocyanate, AuSCN + AgSCN. Ammonia also produces a white precipitate of aur-ammonium thiocyanate $(AuNH_3)SCN$.

AURIC SALTS.

597 *Auric Chloride,* or *Gold Trichloride,* $AuCl_3$. Geber and all the later chemists were acquainted with the fact that gold dissolves in aqua-regia. When this solution is evaporated to dryness a portion of the chloride is decomposed with formation of aurous chloride (Berzelius). In order to prepare the pure anhydrous chloride the best process is that proposed by Thomsen. It consists in acting upon gold powder with chlorine when the dichloride, $AuCl_2$, is formed. This is a dark-red crystalline powder which, when mixed with a small quantity of water, is converted into the trichloride and monochloride. When gently heated the latter decomposes as before described, the metallic gold is filtered off, the solution evaporated gently, and then heated to 150°, when anhydrous auric chloride remains as a brown crystalline mass. The anhydrous chloride is also formed by heating gold-leaf in chlorine to 300°, and it sublimes in a stream of chlorine in reddish crystals.[2] When the brownish-

[1] Elsner, *Journ. Pract. Chem.* xxxvii. 333.
[2] Debray, *Compt. Rend.* lxix. 985.

red aqueous solution is evaporated down until a crystalline film is formed on the surface, large dark orange-red crystals are deposited of $AuCl_3 + 2H_2O$. These deliquesce in moist air, whilst they effloresce in dry air.

Chlor-auric Acid. When hydrochloric acid is added to a neutral solution of auric chloride it becomes yellow and the liquid then contains the above compound in solution. The same substance is obtained when gold is dissolved in aqua-regia containing an excess of hydrochloric acid. When either of the above solutions are evaporated and allowed to stand over quicklime, long yellow needles of $HAuCl_4 + 4H_2O$ are deposited, which deliquesce on exposure. The solution has a bitter taste, is poisonous, and colours the skin, nails, ivory, &c., of a purple-red tint when exposed to light. This fact was mentioned in 1663 by Boyle as being one then not generally known.

Gold chloride not only combines with hydrochloric acid, but with many other soluble chlorides to form soluble compounds. For this reason the above hydrochloric acid compound is regarded as a peculiar acid, termed Chlor-auric Acid.

Potassium Chlor-aurate, $KAuCl_4$. When the strongly acid solution of gold chloride, to which the calculated quantity of potassium chloride has been added, is allowed to evaporate at a gentle heat, light-yellow monoclinic needle-shaped crystals, having the composition $2KAuCl_4 + H_2O$ are deposited. On the other hand, when the neutral or slightly acid solution is employed, large transparent rhombic tables of $KAuCl_4 + 2H_2O$ are formed, which easily effloresce on exposure. When heated these melt with evolution of chlorine, forming a dark-brown liquid, which on cooling turns yellow, with formation of the salt $KAuCl_2$. This is decomposed by water into gold, potassium chloride, and potassium chlor-aurate.

Sodium Chlor-aurate, $NaAuCl_4 + 2H_2O$, is obtained by dissolving common salt in a solution of gold chloride and concentrating the solution, when it is deposited in yellowish-red rhombic tables or prisms, which do not alter on exposure.

Ammonium Chlor-aurate, NH_4AuCl_4, appears to have been prepared by Basil Valentine, who employed aqua-regia containing sal-ammoniac for dissolving the gold, and on cooling the solution obtained crystals which he considered to be a true gold vitriol. From the neutral solution large light-yellow rhombic tables of the composition $2NH_4AuCl_4 + 5H_2O$ separate. These are tolerably permanent. From an acid solution, on the other

hand, the salt $4NH_4AuCl_4 + 5H_2O$, crystallizes in monoclinic plates. Both salts become anhydrous at 100°.

The chlorides of the calcium and magnesium groups, as well as those of manganese, nickel, cobalt, xantho-cobalt, and thallium also form crystalline chlor-aurates.

598 *Auric Bromide*, or *Gold Tribromide*, $AuBr_3$. Finely-divided gold dissolves slowly in hydrobromic acid (Balard). In order to obtain the anhydrous compound, bromine is allowed to act upon gold powder, when the black compound Au_4Br_2 is formed, from which the tribromide is extracted by ether. When the solution is evaporated at a low temperature, the tribromide remains behind as a black crystalline crust, which dissolves slowly in water. The concentrated solution is viscid and almost black (Thomsen).

Brom-auric Acid, $HAuBr_4 + 5H_2O$, is formed when bromine is allowed to act upon gold powder, and as soon as the reaction is over, a quantity of hydrobromic acid, having a specific gravity of 1·38, equal to the quantity of gold present, is added, and then bromine again added until the gold is completely dissolved. It crystallizes in dark cinnabar-red flat needles.

Auric Iodide, AuI_3. When a neutral solution of gold chloride is added to one of potassium iodide, the liquid becomes of a dark-green colour, and yields a green precipitate, which on agitation dissolves again, inasmuch as potassium iod-aurate is formed. If, however, more gold solution is added, a permanent precipitate is formed, and this, after washing, may be dried, but it evolves iodine, and is converted on standing into aurous oxide.[1] It forms dark-coloured compounds with the soluble iodides.

Potassium Auric Sulphite, $5K_2SO_3 + Au_2(SO_3)_3 + 5H_2O$, is formed when potassium sulphite solution is poured into a solusion of potassium aurate, the above salt separating from the brown liquid in beautiful yellow needles. It is very unstable, and easily decomposes with separation of gold.

Auric Cyanide, $Au(CN)_3$, is not known in the free state, but exists in combination with hydrocyanic acid and other cyanides.[2]

Cyan-auric Acid, $HAu(CN)_4 + 6H_2O$, is obtained from the potassium salt by precipitation with silver nitrate. The precipitate is washed with cold water and decomposed by somewhat less than the requisite quantity of hydrochloric acid. The

[1] Johnston, *Phil. Mag.* [3], ix. 266.
[2] Himly, *Ann. Chem. Pharm.* xlii. 340; and Gmelin, *Handbook*, viii. 41.

filtrate yields on evaporation tabular crystals which are easily soluble in water, alcohol, and ether.

Potassium Cyan-aurate, $2KAu(CN)_4 + 3H_2O$, is obtained by mixing hot concentrated solutions of gold chloride and potassium cyanide. On cooling it crystallizes in large colourless tables, which usually effloresce. It is used for electro-gilding.

Ammonium Cyan-aurate, $NH_4Au(CN)_4 + 2H_2O$, is formed by dissolving the hydroxide in ammonium cyanide and crystallizing by spontaneous evaporation. It forms either four- or six-sided tables, which are easily soluble in water and alcohol, but not in ether.

Auric Thiocyanate is not known in the free state, but if a solution of gold chloride be precipitated by potassium thiocyanate in the cold an orange-yellow precipitate of $KAu(SCN)_4$ is thrown down, which crystallizes in fine needles from warm water with partial decomposition.

AURATES.

599 *Potassium Aurate,* $KAuO_2 + 3H_2O$, is obtained by evaporating a solution of auric hydroxide in caustic potash in a vacuum in the form of small yellow needles, easily soluble in water and having a strong alkaline reaction. It is very unstable, and its solution is used for gilding copper and other metals.

The other aurates are less completely investigated. The solution of the potassium salt yields precipitates with many metallic salts. Some of these, such as that formed with calcium chloride, dissolve in an excess of the precipitant.[1]

GOLD AND SULPHUR.

600 *Gold Disulphide,* Au_2S_2, is obtained as a hydrated black precipitate when sulphuretted hydrogen is passed into a cold solution of the chloride.[2] It dissolves in the sulphides of the alkali metals, and is easily decomposed into its elements, from which it appears that gold does not combine directly with sulphur. If, however, gold be fused with the polysulphides of the alkali metals, double sulphides are formed, of which that of sodium is best known.

[1] Fremy, *Ann. Chim. Phys.* [3], xxxi. 480.
[2] Levol, *Ann. Chim. Phys.* [3], xxx. 355.

Sodium Auro-sulphide, $NaAuS + 4H_2O$, is obtained by heating gold with sodium sulphide and sulphur, and treating the fused mass with water. The solution must be filtered in an atmosphere of nitrogen, and evaporated in a vacuum over sulphuric acid. Colourless monoclinic prisms are then deposited, which soon become brown on exposure to air. The same salt is obtained by dissolving gold sulphide in a solution of sulphide of sodium.

That gold can be brought into solution by fusing it with liver of sulphur seems to have been known to Glauber, but Stahl in his *Observationes Chymico-physico-Medicæ* is the first distinctly to mention this fact; and, it may be added that he there explains that Moses burnt up the golden calf with alkali and sulphur, and gave the solution of liver of sulphur containing gold to the Israelites to drink.

GOLD AND PHOSPHORUS.

601 When gold is greatly heated in phosphorus vapour the compound Au_2P_3 is formed as a grey mass possessing a specific gravity of 6·6, and easily losing phosphorus when more strongly heated. It is not attacked by hydrochloric acid, but is decomposed by nitric acid, the phosphorus being dissolved and the gold left (Schrötter).

Gold combines with arsenic, antimony, and bismuth when heated with these elements. The addition of 1 part of the latter metal to 1,920 parts of gold is sufficient to render the gold brittle.

Detection and Estimation of Gold.

602 When a gold compound is heated on a carbonized match in the reduction flame a yellow malleable bead is obtained which dissolves in aqua-regia. If this solution be dropped on to filter paper and one drop of stannous chloride added, a purple-red colour is observed. Gold can be readily detected in its solutions, inasmuch as it is obtained in the metallic state by reducing agents, the well-washed precipitate being dissolved and the solution tested with stannous chloride. The separation of gold from the other metals will be described under the head of Platinum.

The spark-spectrum of gold has been mapped by Kirchhoff,

Thalén, and Huggins. The brightest lines are 6,275, 5,961, 5,956, and 5,838 in the orange and yellow, and 5,230, 4,792 in the green and blue. Gold compounds do not impart any tint to the non-luminous gas-flame.

603 *Assay of Gold.* In quantitative analysis gold is always weighed in the metallic state. In order to determine the value of commercial gold for the purposes of the goldsmiths or for the coinage, it is cupelled with lead with addition of so much silver that the quantity of the latter is about two-and-a-half times that of the gold present. A gold-silver alloy is thus obtained, which is rolled into foil, and then boiled with nitric acid of specific gravity 1·08. The residual gold cornet having been well washed is placed in a small crucible, and heated in a muffle to a point just below that at which gold melts, in order to render it coherent, after which it is cooled and weighed.

The assaying of gold is an operation of much importance, and one in which great accuracy is needed. The errors attaching to the process are chiefly (1) errors in weighing, (2) loss of gold by absorption in the cupel and by volatilisation, (3) slight solution of the gold by impurity in the acid, (4) and most important, the presence of a portion of the silver in the gold cornet.

The degree of accuracy which can be reached by this process depends not only upon the skill of the operator, but upon an elimination of the above sources of error. This can be attained, provided that the process is conducted with perfect uniformity in all cases, by assaying one sample of gold alloy of exactly known composition, and correcting the assays made of the other samples in a corresponding ratio. The Bank of England carry on their enormous transactions in bullion upon triple assays of each ingot made by some scientific assayer of high standing, as single assays are liable to accidents or mistakes; and in every mint two or more assayers are employed to check each other's results. Such check assays ought not to differ among themselves more than ten or twenty parts out of 10,000 of gold.[1]

The *atomic weight* of gold was first determined by Berzelius [2] by ascertaining the quantity of mercury necessary in order to precipitate gold from its chloride, and the mean of two experiments gave him the number 196·69. At a later period he determined the relation between gold and potassium chloride in potassium chloro-aurate, $KAuCl_4$, and obtained the number

[1] W. S. Jevons, article "Gold-Assay," *Watts's Dictionary.*
[2] *Schweigg. Journ.* vii. 44.

196·33,[1] whilst Levol [2] got 195·7 by reducing a solution of the pure auric chloride by sulphur dioxide and determining the relation between the precipitated gold and the sulphuric acid which was formed by the reduction.

PLATINUM. Pt = 196·7.

604 This metal appears to have been first observed in the sixteenth century, for Scaliger, who died in 1558, in his work *Exercitationes Exotericæ de Subtilitate*, combated the views of Cardanus that all metals are fusible, for, he adds, in the mines of Mexico and Darian a metallic substance is found "quod nullo igni, nullis Hispanicis artibus, hactenus liquescere potuit." As platinum occurs in the above districts it appears very probable that this was the metal here referred to.

It was not, however, until two centuries later that platinum again attracted attention, and this time many chemists occupied themselves diligently with the subject. The first of these was Don Antonio de Ulloa, who took part in the French Expedition of 1735 which had for its object the measurement of an arc of the meridian on the equator. In 1748 he published his *Relacion Historica del Viage a la America Meridional*, in which he describes an unworkable metallic mineral which even makes gold ore useless if it occurs mixed with it in large quantities. William Watson [3] was the first to describe native platinum as a compact metal. He had obtained it nine years previously from Charles Wood, who had brought some samples of it from Carthagena in Granada to Jamaica, and thence to England. Watson termed it a semi-metal. It was afterwards more exactly examined by Scheffer, who describes it in the Memoirs of the Stockholm Academy in 1752 with the title "On White-gold or the seventh Metal, termed in Spanish 'platina del Pinto,'" that is, small silver of Pinto, *platina* being the diminutive of *plata*, the Spanish for silver. The name of del Pinto was added because it was first found in the auriferous sand of that river. Scheffer describes the insolubility of platinum in nitric acid, and was acquainted with the facts that aqua regia dissolves it and that it is precipitated from the solution by mercury. He also states that it is infusible at the strongest heat of a furnace, but that it

[1] *Berz. Jahresb.* xxv. 41. [2] *Ann. Chim. Phys.* [3], xxx. 355.
[3] *Philosophical Transactions* for 1750.

can be alloyed with other metals, and that it may be fused by the help of arsenic. He declares the new body to be a true metal, and, on account of its unalterability, believes it to be a noble one, and suggests that it may be used for the speculæ of telescopes. In 1754 Lewis[1] published a series of researches on platinum, and in 1757 the investigations of Marggraf were communicated to the Berlin Academy. Amongst the most important of his observations was that which has since proved of such service to analytical chemistry, that platinum solution produces with the salts of the alkalis an orange-yellow precipitate, with the exception of that of the mineral alkali soda, with which it produces none. Next came Macquer and Baumé's researches on platinum, which were published in the Memoirs of the Paris Academy for 1758. The most important new fact observed by these chemists was that platinum can be fused in the focus of a powerful burning-glass. Besides this, the paper in question contains the information that platinum had hitherto been so rare a substance because the Spanish Government had forbidden the export of platinum, inasmuch as gold could be alloyed with a considerable quantity of the new metal without its colour being sensibly changed, thus giving rise to the possibility of fraud. Further investigations were made by Cronstedt in 1764 and by Bergmann in 1777, the latter chemist explaining the nature of the changes which occur when a platinum solution is treated with the alkalis. Count von Sickingen, at that time the representative of the Palatinate at the Court of Paris, worked diligently on the subject of platinum and was the first, in 1772, to prepare platinum foil and platinum wire, and to show that this metal dissolves in nitric acid when alloyed with silver. His experiments were communicated to the Academy in 1778, and in 1782 the same researches were described in a pamphlet which appeared in German with the title *Experiments on Platinum*. The whole of the preceding researches, as well as many of those carried on at a later time, were made with South American platinum.

In 1819 grains of a white metal were discovered in the auriferous sands of the Urals, but it was not till 1823 that platinum was detected in this substance. This discovery gave rise to the Scientific Expedition to the Urals undertaken by Humboldt, G. Rose and Ehrenberg, in 1829.

Platinum occurs only in the native state, but native platinum

[1] *Phil. Trans.* 1754, 638.

is very seldom pure, the purest specimens having been found in Brazil together with grains of palladium. The usual platinum "ore," as it is termed, contains all the metals of this group together with iron, copper, titanic iron ore, &c. It is sometimes, though seldom, found crystallised in cubes and octohedrons, but more usually occurs in rounded or flattened grains or sand having a metallic lustre, and occasionally in large rounded nuggets, both forms occurring in river sand or detritus. Some of the more important localities from which platinum is obtained are, Choco near Popayan in New Granada, the gold-washings of the Pinto in the province of Antioquia, and Minos Geraes in Brazil. In the Urals it is found in alluvial deposits at Nischnetagilsk and Goro-blagodat. Platinum likewise occurs in the Natoos Mountains in Borneo, which annually furnish some 600 to 800 pounds, and in Haiti, Peru, California, India, and Australia. It is also found in small quantities in the sands of various rivers, occurring in the Rhine, and in streams in Wicklow, North Carolina, and Canada East. The largest mass which has yet been obtained is that in the Demidoff Cabinet in St. Petersburg weighing 7·837 kilos. In the Urals platinum is found together with chrome-iron ore in serpentine, whilst in the Brazils it occurs with gold in syenite. Many common minerals such as dolomite, heavy spar and fahl ore, &c., contain traces of platinum, and this explains the occurrence of the metal in the sands of so many rivers. It is also found in small quantities in most of the ores of lead and silver, and it is usually contained with palladium in small quantities in all silver.

605 *The Metallurgy of Platinum.* The infusibility of platinum, as well as its power of withstanding the action of many of the most powerful reagents, rendered it desirable that this metal should be employed for the manufacture of vessels for chemical use. In 1784 Achard mentioned that the substance obtained by fusing arsenic and platinum together leaves, on ignition, a residue of malleable platinum, and in this way he prepared what was in all probability the first platinum crucible. This method was employed from the year 1787 in Paris, where Jannetty was celebrated for his platinum work. Platinum vessels were, however, then and for some time afterwards so expensive and difficult to obtain, that in the year 1801 G. Rose and Karsten, for want of a platinum crucible, were unable to examine the statement of Guyton de Morveau and Desormes that potash consists of lime and hydrogen, and soda of magnesia and hydrogen.

The following table contains a series of analyses of various platinum ores by Deville and Debray:[1]

Locality . . .	Choco (S. America).	California.	Australia.	Ural.
Platinum . .	86·20	85·50	61·40	76·40
Gold	1·00	0·80	1·20	0·40
Iron	7·80	6·75	4·55	11·70
Iridium . . .	0·85	1·05	1·10	4·30
Rhodium . .	1·40	1·00	1·85	0·30
Palladium . .	0·50	0·60	1·80	1·40
Copper . . .	0·60	1·40	1·10	4·10
Osmiridium. .	0·95	1·10	26·00	0·50
Sand	0·95	2·95	1·20	1·40
	100·25	101·15	100·20	100·50

The body termed osmiridium is an alloy of osmium and iridium which is not attacked by aqua-regia, and the sand contains quartz, chrome-iron ore, hyacinth, spinelle, and titanic iron.

In the year 1800 Richard Knight[2] published a method for preparing malleable platinum. This consisted in dissolving the crude platinum, precipitating the solution with sal-ammoniac, stamping the dried precipitate of the double chloride of platinum and ammonium into a conical mould made of fire-clay, and igniting the whole. In this way platinum is obtained as a coherent metallic mass, which can then be worked up. In 1822 a similar method was described by Barrual, but for many years before this, in fact from 1800 to 1809, a relative of a present member of the well-known firm of Messrs. Johnson, Matthey, and Co., was employed in working on platinum, and had discovered (whether independently of Knight is uncertain) a method for consolidating the sponge, which was afterwards elaborated by Wollaston and described by him in the Bakerian Lecture[3] for 1828. This, although identical in the main features with Knight's process, is distinguished from it in several important particulars, and is the process by which platinum was manufactured up to the year 1859, when Deville's process came into use.[4] Wollaston in the first place pointed out the necessity of heating the double chloride very

[1] *Ann. Chim. Phys.* [3], lvi. 449.
[2] *Tilloch's Phil. Mag.* vi. 1.
[3] *Phil. Trans.* 1829, p. 1.
[4] *Ann. Chim. Phys.* [3], lvi. 484.

gently at a temperature just sufficient to expel the whole of the sal-ammoniac and to occasion the particles of platinum to cohere as little as possible, for on this depends the ultimate ductility of the product. The metallic powder thus obtained must be rubbed between the hands of the operator so fine as to pass through a fine lawn sieve. After having been well levigated, the uniform mud or pulp is pressed whilst cold into a brass barrel and strongly compressed by a powerful lever. The cake of platinum can be easily removed owing to the conical form of the barrel, and is now so hard that it can be handled without danger of breaking. It is then placed on a charcoal fire, and heated to redness to drive off moisture and to give it a greater degree of cohesion. After this it is heated in a wind furnance to the most intense heat that can be obtained. After ignition for about twenty minutes, the cake is removed from the furnace and placed upright on an anvil, and struck when hot on the top with a heavy hammer. The ingot of platinum thus obtained may be drawn into wire or submitted to any of the processes of which the most ductile metals are capable.

The easy method thus proposed for working up platinum has had a great influence on the progress of chemistry. The present generation of chemists can scarcely understand the difficulties which their predecessors had to contend with, unable, as they were, to use either platinum crucibles, basins, retorts, or platinum foil or wire. In his *Letters on Chemistry* Liebig says:

"Without platinum it would be impossible, in many cases, to make the analysis of a mineral. The mineral must be dissolved, and it must be first rendered soluble, or prepared for solution. Now, vessels of glass, of porcelain, and of all non-metallic substances are destroyed by the means we employ for that purpose. Crucibles of gold and silver would melt at high temperatures. But platinum is cheaper than gold, harder and more durable than silver, infusible at all temperatures of our furnaces, and is left intact by acids and alkaline carbonates. Platinum unites all the valuable properties of gold and of porcelain, resisting the action of heat, and of almost all chemical agents. Without platinum the composition of most minerals would have yet remained unknown."

Platinum apparatus is also employed on a large scale and with great advantage in the chemical industries; thus, for example, in the manufacture of sulphuric acid, in the parting of the noble metals, and in the preparation of oxygen on the large scale

by the process of Deville and Debray. The first platinum apparatus for concentrating sulphuric acid, weighing 423 ounces, was made in London in 1809 by the well-known firm of Messrs. Johnson, Matthey, and Co., who since that time have furnished platinum vessels for all parts of the world.

In the year 1807 the quantity of platinum ore which had accumulated in the St. Petersburg Mint was considerable, and the experiment of coining with platinum was tried. The coinage of platinum was, however, soon abandoned, and the coins in circulation were withdrawn, owing to the very considerable variations which the price of the metal undergoes from year to year, and the impossibility therefore of fixing a permanent monetary value upon the coin. The quantity of platinum raised yearly in Russia amounts to about 800 cwt., which is nearly ten times the quantity obtained from Brazil, Columbia, San Domingo and Borneo. The value of platinum coined in Russia from 1826 to 1844 amounted to 2,500,000 dollars. How variable the annual production of platinum ore is will be seen from the following numbers: in 1862 the quantity raised was 142 puds 1 lb.; in 1863, 30 puds 2 lbs.; in 1864, 24 puds 9 lbs.; in 1865, 138 puds 32 lbs.; in 1867, 107 puds 38 lbs.; in 1871, 125 puds 6 lbs.—1 pud being equal to 40 lbs. or 16·38 kilos.

606 The application of the oxyhydrogen blowpipe for fusing large masses of platinum proposed first by Hare[1] has exerted a great influence on the progress of the platinum industry. Hare succeeded in fusing 971 grams of platinum as well as large quantities of iridium and osmium. This method was improved upon by Deville and Debray,[2] whose investigations on the platinum metals have been of service to the general progress of chemical industry. The means employed by these chemists for fusing platinum, and now employed on the large scale by most of the platinum manufacturers, consists in the use of two well-fitting lumps of quicklime. The upper one has a hole drilled through the middle for the introduction of the blowpipe, whilst a side opening permits the escape of the products of combustion and serves as an outlet for the molten metal. Instead of hydrogen common coal-gas is usually employed. This is allowed to enter through the tube H, Fig. 169, whilst the oxygen enters at O. The upper portion of the blowpipe consists of copper and the lower of platinum. Lime is used for the crucible, because it stands a

[1] *Phil. Mag.* [3], xxxi 356. [2] *Ann. Chim. Phys.* [3], lvi. 385.

high temperature well, and at the same time it absorbs the slags of the oxides of iron and silicon and other materials which are formed during the operation. The introduction of this process induced chemists to seek for a cheap method of preparing oxygen on the large scale (Vol. I. p. 177), whilst by means of the oxy-hydrogen blowpipe Messrs. Johnson, Matthey, and Co. have succeeded in effecting a most important improvement in the metallurgy of platinum, viz. that of soldering platinum by itself (autogenous soldering), instead, as was formerly the case, of soldering with gold.

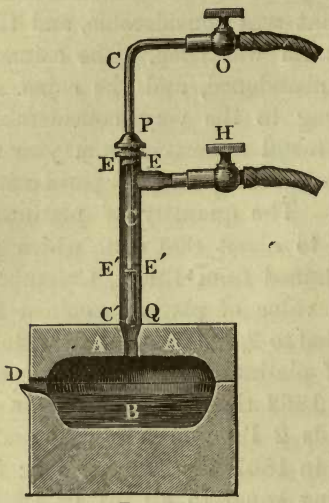

FIG. 169.

Deville and Debray have also endeavoured to introduce a direct process for obtaining platinum from its ores in the dry way, and thus to replace Wollaston's tedious process of preparation. For this purpose they have suggested two processes.[1] According to the first of these the ore, after having been mixed with lime, is simply fused. In this way an alloy of platinum with iridium and rhodium is obtained. This method is especially applicable to the fusion of old platinum vessels, inasmuch as all the impurities, such as sulphur, phosphorus, iron, gold, lead, &c., which occur in the scrap-platinum, are either volatilized or absorbed by the lime. The second method depends on the fact that lead can be alloyed with the platinum metals but not with osmiridium. The platinum ores always contain iron, and hence galena is employed instead of metallic lead, and glass and borax are added as fluxes. This operation is carried out in an ordinary melting crucible. The osmiridium which does not alloy with the lead is allowed to deposit by its higher specific gravity, and litharge gradually added until no further evolution of sulphur dioxide takes place. After cooling, the osmiridium, which remains at the bottom, is separated from the upper mass, the lead alloy cupelled, and the remaining platinum, containing a small quantity of iridium and rhodium, fused in a

[1] *Ann. Chim. Phys.* [3], lvi. 385; lxi. 5.

lime crucible with the oxyhydrogen blowpipe. These processes have, however, not met with much success in practice, inasmuch as there is no guarantee that the platinum thus prepared does not contain, in addition to the iridium and rhodium which are harmless constituents, other admixtures, or that the metal thus obtained is homogeneous. Hence up to the present time Wollaston's process of preparation by the wet way is universally made use of. The following process for this purpose is adopted in the German works of Heräus in Hanau.[1] The raw ore is treated in glass retorts under a pressure of twelve inches of water with a mixture of 1 part of aqua-regia and 2 parts of water. The solution is evaporated to dryness, and the dried mass heated to 125°, at which temperature the palladium and rhodium salts are reduced to lower chlorides. The clear aqueous solution acidified by hydrochloric acid is precipitated with sal-ammoniac, the pure double chloride of platinum and ammonium being thrown down, whilst the corresponding iridium salt is obtained on evaporating the mother-liquor. The solution remaining after precipitating the platinum salt is treated with scrap-iron, when the other metals are thrown down, and the precipitate, from which the excess of iron has been dissolved by hydrochloric acid, again treated with aqua-regia, and from this solution a new portion of platinum and iridium thrown down. The mother-liquors, as well as the residue left on dissolving the ore in aqua-regia, contain the metals palladium, rhodium, ruthenium, osmium, and iridium. The spongy platinum obtained by igniting the double chloride of platinum and ammonium is then pressed, broken up in pieces, and fused with an excess of oxygen in a lime crucible. Most of the platinum which occurs in commerce is not pure, but contains, like Russian platinum coin, 2 per cent. of iridium. This alloy is especially valuable for the preparation of chemical vessels, inasmuch as it is less readily attacked by acids than pure platinum.

607 *Preparation of Pure Platinum.* In order to prepare pure platinum various methods have been proposed. Deville and Debray[2] have prepared it on a large scale by the following process. The metal which contains iridium and rhodium is fused with from six to ten times its weight of lead, the mass after cooling is treated with nitric acid, and the residue treated with dilute aqua-regia, when a crystalline alloy of iridium,

[1] Philipp, *Ber. Entw. Chem. Ind.* i. 999.
[2] *Compt. Rend.* lxxxi. 893.

ruthenium, and iron remains behind, whilst lead, platinum, and some rhodium go into solution. This latter is treated with sal-ammoniac, so that the double chloride $(NH_4)_2PtCl_6$ is thrown down in a finely-divided amorphous state and almost white, and thus the rhodium is kept in solution. The precipitate is washed with water containing hydrochloric acid, ignited, and the residual platinum fused in a lime crucible. When fused the supply of gas is suddenly stopped, so that the metal solidifies from the outside inwards and in this way the formation of bubbles in the metal is avoided.

According to G. Matthey,[1] the preparation of pure platinum is a matter of great difficulty. His process is, to begin with, similar to that already described, but he evaporates down the aqua-regia solution, and then adds pure sulphuric acid to the residue in order to convert any lead which may remain in solution into the insoluble sulphate. The platinic chloride is then dissolved out by water and precipitated by a mixture of sal-ammoniac and common salt; this latter being added because the ammonium platinum chloride is less soluble in a solution of common salt than in water. The liquid is then heated to 80° and allowed to stand for some days in order that the precipitate may become denser. This is then repeatedly washed with solution of sal-ammoniac, and at last with distilled water acidified with hydrochloric acid. The washed precipitate is then dried and mixed with bisulphate of potash to which a small quantity of bisulphate of ammonium has been added. The mixture is then heated to dark redness in a platinum basin. On boiling the mass with water, potassium sulphate and potassium rhodio-sulphate dissolve, leaving pure platinum behind.

608 *Properties.* Pure platinum has a tin-white colour, is soft like copper, has a specific gravity of 21·5, and is the most malleable of metals after gold and silver. Like iron, it can be readily welded at a white-heat, and an extremely fine wire can be melted in the flame of a Bunsen burner, but in large masses it is infusible even at the highest temperature of a blast-furnace; it can, however, be fused in the oxyhydrogen flame. Deville estimates its melting-point at 2,000°. When large masses of the molten metal are quickly cooled, they exhibit the phenomenon of "spitting," so characteristic of silver.

Tubes made from fused and hammered platinum allow hydrogen to pass through them at a strong red-heat in larger

[1] *Proc. Roy. Soc.* 1879.

quantity than is the case with caoutchouc membranes at the ordinary temperature. This property depends upon the fact that the red-hot metal has the power of absorbing hydrogen (Vol. I. p. 105), taking up 3·8 volumes of the gas which it gives off on heating in a vacuum, the surface of the platinum becoming in this case covered with bubbles. The same henomenon is noticed when platinum foil is employed as the negative pole in the electrolysis of water, the absorbed hydrogen being again given off when it is converted into the positive pole.

Oxygen is not absorbed by platinum, but the metal possesses the singular power of condensing this gas on its surface. In January, 1817, Sir Humphry Davy communicated the fact to the Royal Society that mixtures of oxygen or air with hydrogen, carbon monoxide, ethylene, vapour of alcohol, vapour of ether, and other easily inflammable gases or vapours, are capable of bringing about the incandescence of a warmed platinum wire,[1] and that then these mixtures either combine slowly or in some cases quickly, and even with explosion. This now well-known phenomenon is thus described by Davy: "A temperature much below ignition only was necessary for producing the curious phenomenon, and the wire was repeatedly taken out and cooled in the atmosphere till it ceased to be visibly red, and yet when admitted again it instantly became red-hot." In the following year Erman observed that it was only necessary to warm the platinum wire to 50° to enable it to bring about this combination.

In 1820 Ed. Davy showed that the black powder deposited when a platinum solution is precipitated by sulphuretted hydrogen, the precipitate dissolved in nitric acid, and the liquid thus obtained mixed with its own volume of alcohol, possesses the property, when moistened with spirits of wine, of becoming ignited in the air. Two years later Döbereiner observed that spongy platinum, obtained by the ignition of the double chloride of platinum and ammonium, exhibits the same phenomenon when gently warmed with alcohol. In 1823 the same chemist noticed that when hydrogen is allowed to pass over spongy platinum in presence of air, the hydrogen gas is ignited, and upon this was founded the well-known Döbereiner's Hydrogen Lamp.[2] Faraday afterwards showed that chemically clean platinum acts in a similar way. The circumstances under which

[1] *Phil. Trans.* 1817, p. 77.
[2] *Schw. J.* xlii. 60. *Tilloch's Phil. Mag.* lxv. 150.

platinum and certain other metals exhibit this action were investigated by Thénard and Dulong in a research published in the same year.

In order to exhibit this action Davy's glow-lamp is used (Fig. 170). It is fed with a mixture of alcohol and ether; this is ignited in order to heat the spiral of platinum wire to redness. The flame is then blown out, and the mixed vapours of alcohol and ether rising from the moist wick are oxidized, and thus the spiral is kept brightly incandescent. The same phenomenon can be observed if a spiral of platinum-wire be hung in a small test-glass (Fig. 171), on the bottom of which a little ether has been poured. Another mode of showing the same experiment is to heat a small piece of platinum foil in the flame of a Bunsen's lamp, and then quickly to extinguish the flame, allowing the gas to escape. The foil soon begins to glow, and if it be placed near the burner it becomes hot enough to re-ignite the gas; if further removed, the foil continues to glow but the gas is not inflamed.

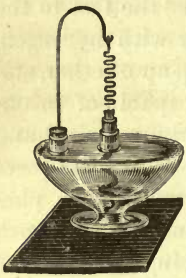

FIG. 170.

FIG. 171.

609 *Spongy Platinum*, first prepared by E. Davy, is very finely-divided metallic platinum, which possesses a very large surface compared with its mass, and is able to condense large quantities of oxygen. This substance is frequently employed as an oxidizing agent, and may be readily prepared by gently heating the double chloride of platinum and ammonium. It then forms a porous mass, which, when heated strongly, becomes denser, and assumes a metallic lustre under the burnisher.

Platinum Black. This form of platinum was also discovered by E. Davy, who, however, misled by certain accidental impurities, considered it to be a platinous nitrite. It is to Liebig[1] that we owe the discovery of this error, and also a description of the best method for the preparation of the substance. This consists in warming a solution of platinum dichloride in potash with alcohol. Thus obtained it is a soft black dull powder, which soils any surface on which it is rubbed. When thoroughly freed from

[1] *Pogg. Ann.* xvii. 102.

alcohol by boiling with water, and dried in a vacuum over sulphuric acid, it absorbs oxygen from the air so rapidly that the mass becomes red-hot. Platinum black is also obtained by dissolving alloys of platinum with other metals, such as copper and zinc, in nitric acid, when the platinum remains in the form of a black powder. This latter preparation, heated in open vessels to a temperature considerably below redness, deflagrates with a hissing noise, sometimes detonating like gunpowder. Platinum black is also obtained when platinum is precipitated by other metals from a dilute solution, or when such solution is treated with reducing agents. Thus, for instance, if a solution of platinic chloride be allowed to drop into a boiling mixture of three volumes of glycerine and two of caustic potash of specific gravity 1·08, the black obtained possesses extremely active properties.[1] According to Liebig, platinum-black absorbs more than 800 times its volume of oxygen. After frequent ignition in a mixture of combustible gas and air, the black becomes denser, approaching spongy platinum in its properties. Platinum-black is frequently used in organic chemistry as an oxidising agent, and lately it has been successfully applied in place of oxide of copper in organic analysis.[2]

Platinum is not oxidised at any temperature by oxygen, water, sulphuric acid, or nitric acid. It is not attacked by sulphur alone, although action takes place if alkalis are present. These latter, as well as nitre, oxidise the metal, and for this reason fusion with alkalis or nitre ought not to be performed in platinum vessels. Alkaline cyanides should not be fused in contact with platinum, as these likewise attack the metal. It is also inadvisable to expose platinum vessels to direct contact with burning charcoal, as the silicon reduced from the charcoal-ash unites with the metal, making it brittle and liable to crack. Especially to be avoided is contact at a high temperature with compounds of the easily reducible metals, as these readily form fusible alloys with the platinum. Phosphorus and arsenic also combine with platinum when heated with it. When platinum vessels are heated over a smoky flame, or in one in which the supply of air is insufficient to bring about complete combustion, the platinum becomes injured owing to formation of a carbide of platinum, which oxidises in the portions of the flame containing an excess of oxygen, and thus blisters the metal.

[1] Zdrawkowitch, *Bull. Soc. Chim.* [2], xxv. 198.
[2] Kopfer, *Journ. Chem. Soc.* 1877. i. 228.

The best method of cleaning a platinum crucible is to fuse in it some bisulphate of potash (Gmelin), and in order to test whether a new platinum crucible is of proper quality it is first boiled with hydrochloric acid, and afterwards with pure nitric acid. If none of the metal is dissolved, the platinum is good.

PLATINUM AND OXYGEN.

610 Two oxides of this metal are known:

Platinum monoxide, or platinous oxide, PtO, giving rise to the platinous salts.

Platinum dioxide, or platinic oxide, PtO_2, giving rise to the platinic salts.

Platinum Monoxide, PtO, is obtained as a grey powder by the careful ignition of the hydroxide, or as a violet powder by igniting the compound of platinic oxide and lime (see p. 401), and treating the residue with nitric acid. When strongly heated it passes into the metal, deflagrating when heated with charcoal. It is reduced to platinum black when heated with aqueous formic acid, CH_2O_2, with violent evolution of carbon dioxide.

Platinous Hydroxide, $Pt(OH)_2$, is obtained by decomposing the dichloride with hot caustic potash. The whole of the chlorine cannot, however, be removed in this way, and if caustic soda be employed, a product is obtained from which the soda cannot be completely washed out (Liebig). It is prepared in the pure state by mixing one part of potassium platinochloride, K_2PtCl_4, with twelve parts of water, adding the exact quantity of dilute caustic soda necessary for decomposition, and heating the mixture to boiling until the alkaline solution has become neutral. It dissolves in hydrochloric, hydrobromic, and sulphurous acids, but not in other oxyacids. Boiling caustic potash decomposes it into metal and the dioxide. It acts as a weak base, of which the haloid salts as well as a few double salts of the oxyacids have been prepared.

Platinum Dioxide, PtO_2, is obtained as a black powder by gently heating the corresponding hydroxide.

Platinum Tetrahydroxide or *Platinic Hydroxide*, $Pt(OH)_4$, is prepared by boiling the solution of platinic chloride with caustic potash when a basic double salt is precipitated, and this is heated with acetic acid in order to dissolve out the

alkali. In this way it is obtained as an almost white precipitate, which on drying becomes yellow, and then possesses the above composition. It dissolves readily in caustic soda and in dilute acids. At 100° it loses its water and assumes an amber colour. Platinic hydroxide acts both as a weak base and as an acid-forming oxide. With bases it yields salts termed *platinates*, of which, however, only the sodium salt has been obtained in the pure state. This possesses the composition $Na_2Pt_3O_7 + 6H_2O$, and is a reddish-yellow, partially crystallized, powder. It is obtained when a clear aqueous mixture of chloroplatinic acid and carbonate of soda is exposed to sunshine, or when the mixture is heated for some time to 100°. The aqueous solution of the two salts may also be evaporated to dryness, and the residue boiled out with water, when a denser precipitate of the same compound is obtained, having an ochre-yellow colour. When an excess of lime-water is added to a solution of platinic chloride, and this exposed to sunlight, a white or yellowish pulverulent precipitate falls down, to which the name of platinate of lime has been given,[1] its composition corresponding approximately to the formula $CaPt_2O_5 + CaCl_2 + 7H_2O$. If the hydroxide be boiled with a solution of a polymolybdate, or a polytungstate, salts of the following acids are formed:

Platinmolybdic acid, $H_8PtMo_{10}O_{36}$.
Platintungstic acid, $H_8PtW_{10}O_{36}$.

These acids and their salts have a yellow or greenish colour, and are crystalline.[2]

THE PLATINOUS SALTS.

611 *Platinous Chloride* or *Platinum Dichloride*, $PtCl_2$, is formed when chloroplatinic acid, H_2PtCl_6, obtained by dissolving the metal in aqua-regia and crystallizing, is heated to 300°, or when spongy-platinum is heated in a current of dry chlorine to between 240° and 250°.[3] It is a greenish-grey powder, having a specific gravity of 5·87, which is not readily moistened with water, and is insoluble in this liquid.

Platinum dichloride unites with phosphorus trichloride to form

[1] Herschel, *Phil. Mag.* i. 58.
[2] Gibbs, *Ber. Deutsch. Chem. Ges.* x. 1384.
[3] Schützenberger, *Ann. Chim. Phys.* [4], xxi. 351.

the compound $PtCl_2PCl_3$, which is obtained by heating spongy-platinum with pentachloride of phosphorus to 250°. The product is easily soluble in benzol or chloroform, and crystallizes from these liquids in fine brown needles. When dissolved in water and the solution evaporated in a vacuum, orange-yellow deliquescent prisms of *chlorplatinophosphorous acid*, $PtCl_2P(OH)_3$, are obtained. This has an acid metallic taste, and yields a white precipitate with silver nitrate and a yellow one with acetate of lead. Corresponding salts of the alkali metals have not been prepared, as hydroxides and carbonates decompose the acid.

The foregoing compound readily takes up another molecule of phosphorus trichloride, forming $PtCl_2(PCl_3)_2$, which may likewise be crystallized from chloroform or benzol in large deliquescent prisms, which melt at 160°, and when strongly heated give off phosphorus trichloride. If these are allowed to remain in contact with water at a winter temperature, or if their solution be evaporated at a low temperature in a vacuum, very deliquescent yellow needles are obtained of *chloroplatinodiphosphorous acid*, $PtCl_22P(OH)_3$, and this readily undergoes decomposition at 12°, with evolution of hydrochloric acid, into the compound $PtClOP_2(OH)_5$. This latter forms white crystals, is less deliquescent than the former compounds, and when heated to 150° is converted into a light-yellow non-deliquescent powder, having the composition $PtClO_2P_2(OH)_3$. The solution of this compound, like the preceding, is precipitated by nitrate of silver.[1]

Carbonyl Chloroplatinites. When platinous chloride is heated to a temperature of 250° in a current of carbon monoxide the following compounds are formed:

$$PtCl_2.CO,$$
$$PtCl_2.(CO)_2,$$
$$PtCl_2.(CO)_3,$$

The last named is produced in largest quantity and is obtained in the pure state by boiling the crude product with carbon tetrachloride. In this way fine orange-yellow needles melting at 130° are obtained and these when heated to from 250° to 260° in dry carbon dioxide yield the first of the above compounds in fine needles which melt at 194° and may be sublimed in a current of dry carbon dioxide at 240° and at 300° decompose into carbonyl chloride, $COCl_2$, and platinum. When this compound, or the

[1] Schützenberger, *Bull. Soc. Chim.* [2], xvii. 482; xviii. 153.

crude product, is heated to 150° in carbon monoxide, the second compound sublimes in white needles which melt at 142°.[1] All these compounds are decomposed by water with separation of the metal and formation of carbon dioxide and hydrochloric acid.

612 *Platinochlorides* or *Chloroplatinites.* The solution of platinous chloride in hydrochloric acid may be regarded as *chloroplatinous acid*, H_2PtCl_4. The potassium salt is the usual starting point for the preparation of this compound and its salts.[2]

Potassium Platinochloride, K_2PtCl_4. This salt, which was first prepared by Magnus,[3] is easily obtained by adding moist cuprous chloride to a thick paste of potassium platinichloride, K_2PtCl_6, and water, in such quantity that a small portion of the platinichloride remains unreduced. On cooling the filtered liquid, the greater portion of the platinous salt separates out, the mother-liquor yielding a second crop on concentration, whilst the remainder of the salt is precipitated from the last portion of the liquor with alcohol. These various crops are then washed with alcohol and the pure salt obtained by recrystallization from hot water. It forms soft rose-coloured crystalline fibres. When the requisite quantity of chloroplatinic acid is added to the hot saturated solution of this salt a precipitate of potassium platinichloride is separated and an almost pure solution of chloroplatinous acid is obtained. This same acid is obtained by treating the barium salt with dilute sulphuric acid. On evaporation in a vacuum over sulphuric acid or caustic potash a solid compound separates out which dries up with loss of hydrochloric acid, forming a brown amorphous mass of $H_2Pt(OH)Cl_3 + H_2O$.[4] By dissolving oxides, hydroxides, carbonates or chlorides in the acid a series of compounds are obtained which have been fully described by Nilson.

Ammonium Platinochloride, $(NH_4)_2PtCl_4$. This salt was first described by Vauquelin and afterwards by Peyronne. It crystallizes from solution in hot water in large red four-sided prisms or in thin tablets.

Most of the other platinochlorides crystallize with water in fine red or brown crystals which are often deliquescent; some such as the silver salt, Ag_2PtCl_4, and the lead salt, $PbPtCl_4$, are flesh-coloured precipitates.

[1] Schützenberger, *Ann. Chim. Phys.* [4], xv. 100, and xxi. 325.
[2] J. Thomsen, *Journ. pr. Chem.* [2], xv. 294.
[3] *Pogg.* xiv. 241.
[4] Nilson, *Journ. pr. Chem.* [2], xv. 260.

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Platinous Bromide, $PtBr_2$, is obtained by heating bromoplatinic acid to 200°. It is a brown mass which dissolves with a brownish-red colour. If boiling saturated solutions of potassium platinochloride and potassium bromide are mixed double decomposition occurs and the potassium chloride may be separated from the *potassium platinobromide*, K_2PtBr_4, by crystallization. The latter forms large nearly black pyramids or brownish-red needles (Thomsen).

Platinous Iodide, PtI_2, is formed by warming the chloride with a solution of potassium iodide. It is a black powder closely resembling lamp-black.

Platinous Sulphite is formed by dissolving the hydroxide in sulphurous acid. On evaporation it remains as a gummy mass the composition of which is not known. It forms, however, several well-defined double salts.

Potassium Platinosulphite, $K_6Pt(SO_3)_4 + 2H_2O$. A solution of potassium platinochloride becomes decolorized when warmed with acid potassium sulphite, the above salt separating out from the solution in yellowish or colourless needles. It is not precipitated by potash or ammonia, and evolves sulphur dioxide only when warmed with hydrochloric acid. Sodium salts precipitate from this solution *sodium platinosulphite*, $Na_6Pt(SO_3)_4 + 7H_2O$, in microscopic needles. If this is dissolved in dilute hydrochloric acid sulphur dioxide is evolved and a yellowish powder, having the composition $Na_2Pt(SO_3)_2 + H_2O$, deposited. This is tolerably soluble in water and reddens litmus faintly.

Ammonium Platinosulphite, $(NH_4)_6Pt(SO_3)_4$. This is obtained as a white crystalline precipitate, when a tolerably concentrated solution of ammonium platinochloride is precipitated with normal ammonium sulphite. When alcohol is added to a solution of chloroplatinic acid decolorized by sulphur dioxide and neutralized by ammonia, white crystals of the compound $(NH_3)_2Pt(SO_3)_2 + H_2O$ are deposited.

PLATINIC SALTS.

613 These are all yellow or brown coloured, possess an acid reaction and an astringent taste.

Platinic Chloride or *Platinum Tetrachloride*, $PtCl_4 + 5H_2O$, is obtained by mixing an aqueous solution of the following compound with silver nitrate in the proportion of one molecule

of platinic chloride to two of silver nitrate, when a precipitate of silver platinic chloride is formed, whilst the yellowish-red solution free from silver yields on evaporation over sulphuric acid fine large red apparently monoclinic crystals possessing the above composition. They are not deliquescent and their concentrated solution is precipitated with sal-ammoniac on standing.[1]

Chloroplatinic Acid, H_2PtCl_6. This compound, which is usually called platinum chloride, is obtained by dissolving the metal in aqua-regia and evaporating with hydrochloric acid until all nitric acid is removed. It crystallizes in brownish-red very deliquescent prisms having the composition $H_2PtCl_6 + 6H_2O$. If the solution be repeatedly evaporated with aqua-regia nitrosoplatinic chloride, $(NO)_2PtCl_6$, is formed. This crystallizes in small orange-coloured cubes and is very deliquescent, dissolving in water with evolution of nitric oxide, the nitrogen trioxide which is at first evolved being decomposed by water.

The hydrogen in chloroplatinic acid can be readily replaced by metals and thus a series of crystalline salts termed the *chloroplatinates* or the *platinichlorides* are obtained, of which the most important are those of the alkali metals, their widely differing solubilities rendering them very valuable in analytical chemistry.

Potassium Platinichloride or *Potassium Chloroplatinate*, K_2PtCl_6, is thrown down, on the addition of potash or one of its salts to the acid, in the form of a yellow crystalline precipitate which is deposited from solution in hot water in the form of small reddish-yellow octohedrons having a specific gravity of 3·586. One hundred parts of water dissolve, according to Bunsen and Kirchhoff, as follows:

At 0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
0·70	0·90	1·12	1·41	1·76	2·17	2·61	3·19	3·79	4·45	5·18 parts.

It is insoluble in a saturated solution of potassium chloride as well as in alcohol. It dissolves in caustic potash and is precipitated from the solution on the addition of acids.

Sodium Platinichloride, $Na_2PtCl_6 + 6H_2O$, is obtained by evaporating the acid with common salt, when light-red triclinic prisms or tables are deposited which have a specific gravity of 2·499. These become anhydrous at 100° falling to a yellowish-red powder, which is easily soluble in water and alcohol.

[1] Norton, *Journ. Chem. Soc.* xxv. 680.

Lithium Platinichloride, $Li_2PtCl_6 + 6H_2O$, crystallizes in large orange-yellow plates which effloresce in the air and are easily soluble in water and in a mixture of alcohol and ether, but not in pure ether.

Rubidium Platinichloride, Rb_2PtCl_6, closely resembles the potassium salt but is still more insoluble, for 100 parts of water dissolve according to Bunsen the following amounts:

20°	40°	60°	80°	100°	
0·141	0·166	0·258	0·417	0·634	parts.

Cæsium Platinichloride, $CsPtCl_6$, is the least soluble of the chloroplatinates of the alkali metals, 100 parts of water dissolving:

20°	40°	60°	80°	100°	
0·070	0·142	0·213	0·291	0·377	parts.

It forms, like the rubidium salt, microscopic glistening honey-yellow transparent regular octohedrons.

Ammonium Platinichloride, $(NH_4)_2PtCl_6$, is obtained by precipitating the acid with an ammonium salt, as a lemon-yellow crystalline powder, which crystallizes from hot-water in orange-yellow octohedrons, having a specific gravity of 3·0, and are undistinguishable in appearance from the potassium salt. One hundred parts of water dissolve at the ordinary temperature about 0·666, and at 100° 1·25 parts of the salt. It is not soluble either in alcohol or ether, and scarcely soluble in a solution of sal-ammoniac. On heating it decomposes without fusion, leaving pure platinum-sponge behind.

Platinic Bromide, $PtBr_4$, has not been prepared. When platinum is dissolved in a mixture of nitric and hydrobromic acids, and the concentrated solution allowed to evaporate over quicklime, dark-red monoclinic prisms of *bromoplatinic acid*, $H_2PtBr_6 + 9H_2O$, are deposited, which are very deliquescent. This compound gives rise to a series of bromoplatinates corresponding to the chloroplatinates, most of which possess a red colour.

Platinic Iodide, PtI_4, is a black or brownish-black amorphous powder obtained by the action of hydriodic acid on a soluble chloroplatinate. This dissolves in hydriodic acid, and the purple-red solution, which becomes of a reddish-black on evaporation in a vacuum, deposits fine reddish-black feathery needles, or brownish apparently monoclinic crystals, having a metallic lustre, of *iodoplatinic acid*, $H_2PtI_6 + 9H_2O$. This easily

decompose into water, hydriodic acid, and platinic iodide. The iodoplatinates are brown and possess a metallic lustre; they are soluble in water and are very unstable, giving off iodine at a temperature below 100°.

Platinic Sulphate, $Pt(SO_4)_2$, is obtained as a brown mass by acting on the hydroxide or chloride with sulphuric acid and evaporating the solution. If ammonia be added to the solution and the precipitate boiled with caustic potash, or if ammonium platinichloride be decomposed by the same reagent, a brown precipitate of *fulminating platinum* is obtained. This probably possesses the composition $Pt_2O_3(NH_3)_3$; it does not explode by percussion or friction, but does so when heated, especially if the rise of temperature be rapid.

PLATINONITRITES.

614 These singular compounds, which do not comport themselves as double salts, were first described by Lang[1] and afterwards investigated more completely by Nilson.[2]

Potassium Platinonitrite, $K_2Pt(NO_2)_4$, is obtained when solutions of potassium nitrite and potassium platinochloride are warmed together. It is deposited in the form of small glistening six-sided prisms, which dissolve in 27 parts of water at 15°, and at a higher temperature in a smaller quantity. Alkalis do not precipitate platinum oxide, and sulphuretted hydrogen does precipitate sulphide of platinum from its solution. When the solution is allowed to evaporate spontaneously, rhombic tables having the composition $K_2Pt(NO_2)_4 + 2H_2O$ separate out. These effloresce readily.

Ammonium Platinonitrite, $(NH_4)_2Pt(NO_2)_4 + 2H_2O$, crystallizes in glistening prisms, which do not undergo alteration in the air, but decompose when heated with evolution of light and heat.

Silver Platinonitrite, $Ag_2Pt(NO_2)_4$, is obtained when solutions of the potassium salt and silver nitrite are mixed. On recrystallizing the precipitated salt from hot water, large yellow glistening monoclinic prisms are obtained, which on heating decompose with incandescence and detonation.

Barium Platinonitrite, $BaPt(NO_2)_4 + 3H_2O$, is obtained by decomposing the silver salt with chloride of barium. It crystal-

[1] *Journ. Prak. Chem.* lxxxiii. 415.
[2] *Ber. Deutsch. Chem. Ges.* ix. 1722, x. 934.

lizes from solution in hot water in colourless octohedrons. If this salt be decomposed by dilute sulphuric acid and the solution evaporated in a vacuum over caustic potash, microscopic crystals having the colour of chromium trioxide separate out; these possess, according to Lang, the composition $H_2Pt(NO_2)_4$. Nilson was unable to obtain this compound. The solution yielded, on evaporation, a gummy mass and a green glistening residue, having the composition $H_4Pt_3O(NO_2)_8 + 2H_2O$. On neutralization with potash and evaporation, this yielded the potassium salt $K_4Pt_3O(NO_2)_8 + 2H_2O$ in oblique four-sided glistening light-yellow tablets.

AMMONIACAL PLATINUM COMPOUNDS.

615 Like the salts of cobalt and of mercury, the various platinum salts are capable of forming peculiar basic compounds with ammonia, the constitution of which is yet but imperfectly understood. The first of these compounds was obtained in 1828 by Magnus.[1] By the action of ammonia on platinous chloride he obtained a green insoluble salt having the composition $PtCl_2(NH_3)_2$, which is well known as Magnus's green salt. Gros [2] then obtained a series of light-yellow or colourless salts by the action of nitric acid upon the green salt of Magnus. Reiset [3] and Peyronne [4] independently found that by the action of ammonia on Magnus's green salt, or on platinous chloride, two other series of compounds could be obtained. These were distinguished as the chlorides of Reiset's first and second bases. Peyronne showed that Magnus's salt is a platinochloride of the second base. Further investigations of these compounds and theoretical speculations concerning their constitution have been made by various other chemists.[5]

Twelve series of these compounds are known. They resemble the ammoniacal cobalt compounds, inasmuch as they are basic bodies which form strongly alkaline hydroxides, and they may likewise be considered as consisting empirically of compounds

[1] *Pogg. Ann.* xiv. 242.
[2] Gros, *Ann. Chim. Phys.* [2], lxix. 204.
[3] Reiset, *ibid.* [3], xi. 417, and *Compt. Rend.* x. 870; xviii. 1103.
[4] *Ann. Chim. Phys.* [3], xii. 193, and xvi. 462.
[5] Raewsky, *Ann. Chim. Phys.* [3], xii. 278; Gerhardt, *Compt. Rend.* xxxi. 244; Buckton, *Ann. Chem. Pharm.* lxxxiv. 220; Thomsen, *Ber. Deutsch. Chem. Ges.* iii. 42; Odling, *ibid.* 682; Blomstrand, *ibid.* iv. 673; Cleve, *Bull. Soc. Chim.* [2], vii. 12; xv. 161; xvi. 203; xvii. 289.

of either platinous or platinic salts with several molecules of ammonia. The chlorides of the platinum-ammonias possess the following composition. It is seen that certain series possess an identical composition, but that these differ from one another in properties:

(1) Platosammonium chloride	$PtCl_2(NH_3)_2$.
(2) Platosemidiammonium chloride . . .	
(3) Platomonodiammonium chloride . . .	$PtCl_2(NH_3)_3$
(4) Platodiammonium chloride	$PtCl_2(NH_3)_4$.
(5) Platinammonium chloride	$PtCl_4(NH_3)_2$.
(6) Platinsemidiammonium chloride . .	
(7) Platinmonodiammonium chloride . .	$PtCl_4(NH_3)_3$.
(8) Platindiammonium chloride	$PtCl_4(NH_3)_4$.
(9) Diplatinammonium chloride	$Pt_2Cl_6(NH_3)_3$.
(10) Diplatodiammonium chloride . . .	$Pt_2Cl_2(NH_3)_4$.
(11) Diplatinammonium chloride	$Pt_2Cl_4(NH_3)_4$.
(12) Diplatintetrammonium chloride . . .	$Pt_2Cl_6(NH_3)_8$.

I. PLATOSAMMONIUM COMPOUNDS.

616 These are formed from the corresponding platodiammonium compounds by withdrawal of the elements of ammonium. They are difficultly soluble or insoluble in water, and dissolve again in ammonia, with formation of platodiammonium compounds. They deflagrate on heating.

Platosammonium Oxide, $PtO(NH_3)_2$, is obtained as a greyish mass by heating the corresponding platodiammonium oxide to 110°. When heated to 200° in a retort it gives off water, ammonia, and nitrogen, and leaves metallic platinum. The *hydroxide*, $Pt(OH)_2(NH_3)_2$, is prepared by decomposing the sulphate with baryta water. It is crystalline, readily soluble in water, and possesses a strongly alkaline reaction, acting as a strong base. It precipitates the solutions of many metallic salts, liberates ammonia from the ammoniacal salts, and readily absorbs carbonic acid from the air.[1]

Platosammonium Chloride, $PtCl_2(NH_3)_2$, is obtained by heating the corresponding diammonium salt from 220° to 270°, or by heating it with hydrochloric acid, as well as by boiling Magnus's green salt with ammonium sulphate or nitrate. It is a sulphur-yellow crystalline body, occasionally consisting of microscopic

[1] Odling, *Chem. News*, xxi. 261 and 289.

octohedrons, which dissolves at 0° in 4,472 parts, and at 100° in 130 parts of water. It decomposes on heating into potassium platinichloride, hydrochloric acid, and nitrogen. The whole of the chlorine is gradually precipitated from its solution in the presence of silver nitrate.

Platosammonium Bromide, $PtBr_2(NH_3)_2$, forms a light-yellow precipitate consisting of microscopic needles, and is formed by mixing a solution of the nitrate with one of potassium bromide.

Platosammonium Iodide, $PtI_2(NH_3)_2$, is a yellow powder obtained by boiling an aqueous solution of platodiammonium iodide. It dissolves easily in ammonia, leaving a residue of the last-named compound, and unites directly with iodine to form ammonium iodoplatinate.

Platosammonium Sulphate, $PtSO_4(NH_3)_2 + H_2O$, is obtained by boiling the iodide or chloride with water and silver sulphate. It is white and crystalline, and difficultly soluble in cold, but more readily in hot water. It possesses an acid reaction, and does not part with its water until a temperature is reached at which the salt itself begins to decompose.

Platosammonium Nitrate, $Pt(NO_3)_2(NH_3)_2$, is formed when the chloride or iodide is boiled with silver nitrate. It dissolves pretty readily, though slowly, in hot water, crystallizes in yellow microscopic needles, and has an acid reaction.

Platosammonium Nitrite is obtained by boiling the chloride with a solution of potassium nitrite. It crystallizes from boiling water in small four-sided prisms, which are difficultly soluble in cold water and detonate slightly on heating.

II. PLATOSEMIDIAMMONIUM COMPOUNDS.

617 These compounds, which are isomeric with the preceding, are formed by the direct addition of ammonia to platinous salts. The oxide is not known.

Platosemidiammonium Chloride, $PtCl_2(NH_3)_2$. By the addition of ammonia to a cold solution of platinous chloride in hydrochloric acid a green precipitate is formed which on boiling with water decomposes into the insoluble green salt of Magnus, and a solution of the above salt, which may be obtained on crystallization, in small yellow prisms, dissolving in 387 parts of cold, and in 26 parts of boiling water. If boiled with caustic soda diplatodiammonium hydroxide is formed.

Platosemidiammonium Bromide, $PtBr_2(NH_3)_2$, is obtained, by precipitating the concentrated solution of the nitrate with potassium bromide, in the form of golden-yellow glistening needles, which when washed become red.

Platosemidiammonium Iodide, $PtI_2(NH_3)_2$, is obtained in fine yellow microscopic crystals by precipitating the nitrate with potassium iodide.

Platosemidiammonium Sulphate is prepared by boiling the chloride with water and silver sulphate. It forms hard yellow crystalline crusts, which are difficultly soluble even in boiling water.

Platosemidiammonium Nitrate, $Pt(NO_3)_2(NH_3)_2$. When the chloride is boiled with silver nitrate this compound is obtained in the form of white crusts consisting of small needles.

Platosemidiammonium Nitrite, $Pt(NO_2)_2(NH_3)_2$. When the chloride is boiled with potassium nitrite solution which has been rendered slightly acid by acetic acid, the above salt is obtained in whitish-yellow prisms which are difficultly soluble in boiling water and explode on heating, finely divided platinum remaining behind.

III. PLATOMONODIAMMONIUM COMPOUNDS.

618 The *chloroplatinite* or *platinochloride* of this group, $Pt(NH_3)_3\ PtCl_4$, is obtained in small quantity when ammonium carbonate is added to a boiling very dilute solution of platinous chloride. It crystallizes in small reddish-brown glistening laminæ slightly soluble in cold but more readily in hot water. By decomposing with silver nitrate and concentrating the solution the *nitrate*, $Pt(NH_3)_3(NO_3)_2 + H_2O$, is obtained in yellow crusts. If the concentrated solution of this latter salt be mixed with hydrochloric acid and cooled down with ice the *chloride*, $Pt(NH_3)_3Cl_2$, separates out in small laminæ or prisms which are readily soluble in water. It unites directly with chlorine to form platinmonodiammonium chloride.

IV. PLATODIAMMONIUM COMPOUNDS.

619 The platinochloride of this group is Magnus's green salt, the first of the compound platinum ammonias which was discovered.

Platodiammonium Hydroxide, $Pt(NH_3)_4(OH)_2$, is obtained by

decomposing the sulphate with baryta water and evaporating in a vacuum, when it is obtained as a mass of white needles which melt at 110°, giving off water and ammonia and leaving platosammonium oxide. It deliquesces on exposure and the aqueous solution may be boiled without decomposition. It has a strong alkaline taste, acts as a caustic, rapidly absorbs carbon dioxide from the air, and decomposes the salts of silver and ammonium.

Platodiammonium Chloride, $Pt(NH_3)_4Cl_2 + H_2O$, is obtained by boiling platinous chloride with ammonia until the green precipitate (Magnus's salt) formed in the first instance re-dissolves (Reiset). On evaporation, the solution yields large colourless quadratic crystals which are very friable, possess a saline taste and are perfectly neutral. They dissolve in 4 parts of cold, and more readily in hot water, alcohol precipitating the salt from solution. At 100° they become anhydrous and when strongly heated they give off ammonia and are converted into platosammonium chloride. If the acid solution be mixed with chloroplatinous acid, Magnus's green salt, $Pt(NH_3)_4PtCl_4$, is precipitated and this is also obtained by reducing chloroplatinic acid with sulphur dioxide and saturating the boiling liquid with ammonia. It forms dark-green needles insoluble in water, alcohol, and hydrochloric acid.

Platodiammonium Bromide, $2Pt(NH_3)_4Br_2 + 3H_2O$, is obtained by decomposing the sulphate with barium bromide. It crystallizes in square tables.

Platodiammonium Iodide, $Pt(NH_3)_4I_2$, is obtained in a similar way with barium iodide and crystallizes in pearly scales.

Platodiammonium Sulphate, $Pt(NH_3)_4SO_4$, is prepared by decomposing the chloride with silver sulphate, or sulphuric acid. In the latter case the acid salt is obtained, and this is converted into the normal salt by recrystallization from hot water. It forms small crystalline grains or scales, but may also be obtained in large colourless transparent quadratic prisms which dissolve in 32 parts of cold, and in a smaller quantity of hot water.

Platodiammonium Nitrate, $Pt(NH_3)_4(NO_3)_2$, is prepared by precipitating the chloride with silver nitrate. It crystallizes in long colourless monoclinic needles which dissolve in 10 parts of water and on heating detonates like gunpowder.

Platodiammonium Carbonate, $Pt(NH_3)_4CO_3 + 2H_2O$, is formed on exposing the hydroxide to the air. When the solution is

saturated with carbon dioxide the acid salt, $Pt(NH_3)_4(CO_3)_2H_2$, separates out in crystals which can be heated to 120° without decomposition.

V. PLATINAMMONIUM COMPOUNDS.

620 These are formed from the corresponding platosammonium compounds by oxidation by the members of the chlorine group, or by nitric acid, &c.

Platinammonium Hydroxide, $Pt(NH_3)_2(OH)_4$, falls, as a heavy yellow crystalline powder, when ammonia is added to a boiling solution of the nitrate. The crystals consist of small monoclinic prisms. They are not soluble in water but easily dissolve in hot dilute acids.

Platinammonium Chloride, $Pt(NH_3)_2Cl_4$, is obtained by the action of chlorine on platosammonium chloride suspended in boiling water. It is a heavy lemon-yellow crystalline powder consisting of small quadratic octohedrons. It dissolves in 100 parts of water at 0° and in 34 parts of boiling water. This compound is soluble in boiling potash with evolution of ammonia.

Platinammonium Sulphate, $Pt(NH_3)_2(SO_4)_2 + 3H_2O$, is a yellowish-white crystalline mass obtained by dissolving the basic salt, $Pt(NH_3)_2(OH)_2SO_4 + H_2O$, in dilute sulphuric acid and evaporating. This latter salt is obtained by decomposing the chloride with silver sulphate and forms a straw-yellow-coloured crust made up of needles. It is very insoluble in water.

Platinammonium Nitrate, $Pt(NH_3)_2(NO_3)_4$, crystallizes in oblique four-sided prisms which are insoluble in cold and slightly soluble in hot water, but dissolve readily in warm water containing nitric acid. When the chloride is boiled with a solution of silver nitrate a basic salt $Pt(NH_3)_2(OH)_2(NO_3)_2 + H_2O$ separates out as a yellow crystalline powder. This when dissolved in hot nitric acid yields the normal salt.

VI. PLATINSEMIDIAMMONIUM COMPOUNDS.

621 These are isomeric with the platinammonium compounds, and they are similarly obtained from the platosemidiammonium salts. The hydroxide is unknown.

Platinsemidiammonium Chloride, $Pt(NH_3)_2Cl_4$, is prepared

from the corresponding plato-compound by treatment with chlorine. It is a heavy yellow powder, consisting of six-sided rhombic or hexagonal plates, which on heating to 100° turns green, and is easily decomposed at 240°. At 0° it dissolves in 300°, and at 100° in 65 parts of water. It dissolves in potash with evolution of ammonia, and is not decomposed by concentrated sulphuric acid.

When platosemidiammonium nitrate is treated with chlorine the salt, $Pt(NH_3)_2(NO_3)_2Cl_2$, is formed, and crystallizes in small yellow needles.

VII. PLATINMONODIAMMONIUM COMPOUNDS.

622 These are obtained from the corresponding platomonodiammonium compounds by oxidation.

Platinmonodiammonium Chloride, $Pt(NH_3)_3Cl_4$, is obtained by the action of aqua-regia on platomonodiammonium chloride. It crystallizes in light-yellow glistening rhombic or hexagonal tables, which are tolerably soluble.

If bromine be added to a solution of the nitrate of platomonodiammonium, a bromo-nitrate is obtained, having the composition $Pt(NH_3)_3(NO_3)_2Br_2$; it forms crystalline crusts having a golden-yellow colour.

VIII. PLATINDIAMMONIUM COMPOUNDS.

623 These are obtained from the corresponding platodiammonium compounds.

Platindiammonium Chloride, $Pt(NH_3)_4Cl_4$, is formed when chlorine is led into the corresponding plato-compound, or when platinammonium chloride is dissolved in ammonia, and the excess of ammonia expelled by evaporation. It forms a white crystalline powder, which by slow crystallization may be obtained in transparent regular octohedrons, having a faint yellow colour. It is almost insoluble in water. From its solution silver nitrate precipitates only the half of the chlorine, but on long-continued boiling with an excess of silver nitrate a further decomposition slowly goes on. When bromine is added drop by drop to a boiling solution of this salt, the compound, $Pt(NH_3)_4Cl_2Br_2$, is obtained as a difficultly soluble orange-

coloured crystalline powder, and by the action of sulphuric acid the salt $Pt(NH_3)_4Cl_2SO_4$ is obtained in thin transparent needles.

Platindiammonium Nitrate. If a solution of platodiammonium nitrate be boiled with nitric acid the basic salt $Pt(NH_3)_4(OH)(NO_3)_3$ is formed, crystallizing in colourless oblique prisms. When this is boiled with ammonia, an amorphous powder of $Pt(NH_3)_4(OH)_2(NO_3)_2$ separates out on cooling. Both these nitrates deflagrate on heating. When hydrochloric acid is added to the last salt a heavy white crystalline powder separates out of $Pt(NH_3)_4(NO_3)_2Cl_2$, and the corresponding iodide, $Pt(NH_3)_4(NO_3)_2I_2$, is obtained by the action of iodine on platodiammonium nitrate.

IX. DIPLATINAMMONIUM COMPOUNDS.

624 Of these the iodide only is known, $Pt_2(NH_3)_4I_6$, and this is obtained by boiling platinammonium iodide with potash and treating the resulting yellow powder with hydriodic acid. It is a black amorphous powder which when again treated with potash and hydriodic acid yields the compounds $Pt_4(NH_3)_8I_{10}$ and $Pt_8(NH_3)_{16}I_{18}$.

X. DIPLATODIAMMONIUM COMPOUNDS.

625 The hydroxide, $Pt_2(NH_3)_4(OH)_2 + H_2O$, is formed, as has already been stated, by the action of boiling caustic soda on the platinsemidiammonium chloride. It is a greyish crystalline insoluble powder, which detonates violently when heated. On treatment with hydrochloric acid it is converted into a yellow body, and this on boiling with water yields the chloride, $Pt_2(NH_3)_4Cl_2$, as a black amorphous powder, and this as well as the nitrate, $Pt_2(NH_3)_4(NO_3)_2$, deflagrates when heated.

XI. DIPLATINDIAMMONIUM CHLORIDE,

$Pt_2(NH_3)_4Cl_4 + H_2O$, is the only known compound of this series. It is a yellow amorphous powder, obtained by the action of aqua-regia on the hydroxide of the preceding series.

XII. DIPLATINTETRADIAMMONIUM COMPOUNDS.

626 These compounds have been chiefly investigated by Cleve. By the action of ammonia on platindiammonium iodonitrate the basic salt, $Pt_2(NH_3)_8OI_2(NO_3)_2$, is obtained in yellow microscopic needles. A solution of this salt yields with potassium iodide a black precipitate of $Pt_2(NH_3)_8I_6$, whilst with nitric acid it forms the salt $Pt_2(NH_3)_8I_2(NO_3)_4$, which can be obtained by crystallization from hot water in small reddish-yellow prisms. By double decomposition with silver salts other double nitrates may be obtained. When the basic iodonitrate is boiled with silver nitrate a white difficultly-soluble crystalline powder is obtained of the basic nitrate, $Pt_2(NH_3)_8(OH)_2(NO_3)_4$. This explodes violently on heating, and is converted by nitric acid into the crystalline normal nitrate, $Pt_2(NH_3)_8(NO_3)_6 + H_2O$, which is decomposed on the addition of water. The basic nitrate yields with hydrochloric acid a difficultly soluble basic chloride, $Pt_2(NH_3)_8(OH)_2Cl_4 + H_2O$, crystallizing in microscopic needles.

627 According to Blomstrand and Cleve, the constitution of the foregoing ammoniacal platinum compounds can be represented by the following graphical formulæ, in which R stands for chlorine or other monad element or radical:

I. Platosammonium compounds, . . $Pt\begin{matrix}NH_3R.\\NH_3R.\end{matrix}$

II. Platosemidiammonium compounds, $Pt\begin{matrix}NH_2(NH_4)R.\\R.\end{matrix}$

III. Platomonodiammonium compounds, $Pt\begin{matrix}NH_2(NH_4)R.\\NH_3R.\end{matrix}$

IV. Platodiammonium compounds, . $Pt\begin{matrix}NH_2(NH_4)R.\\NH_2(NH_4)R.\end{matrix}$

V. Platinammonium compounds, . $R_2Pt\begin{matrix}NH_3R.\\NH_3R.\end{matrix}$

VI. Platinsemidiammonium compounds, $R_2Pt\begin{matrix}NH_2(NH_4)R.\\R.\end{matrix}$

VII. Platinmonodiammonium compounds, $R_2Pt\begin{matrix}NH_2(NH_4)R.\\NH_3R.\end{matrix}$

VIII. Platindiammonium compounds, . $R_2Pt\begin{matrix}NH_2(NH_4)R.\\NH_2(NH_4)R.\end{matrix}$

IX. Diplatinammonium compounds, . $\begin{matrix}RPt\begin{matrix}NH_3R.\\NH_3R.\end{matrix}\\|\\RPt\begin{matrix}NH_3R.\\NH_3R.\end{matrix}\end{matrix}$

X. Diplatodiammonium compounds, $\begin{matrix} PtNH_2(NH_4)R. \\ | \\ PtNH_2(NH_4)R. \end{matrix}$

XI. Diplatindiammonium compounds, $\begin{matrix} R_2PtNH_2(NH_4)R. \\ | \\ R_2PtNH_2(NH_4)R. \end{matrix}$

XII. Diplatintetradiammonium compounds, $\begin{matrix} RPt\begin{matrix} NH_2(NH_4)R. \\ NH_2(NH_4)R. \end{matrix} \\ | \\ RPt\begin{matrix} NH_2(NH_4)R. \\ NH_2(NH_4)R. \end{matrix} \end{matrix}$

PLATINOCYANIDES.

628 The potassium salt is formed when a mixture of equal parts of spongy platinum and ferrocyanide of potassium is heated nearly to redness in a crucible, the mass dissolved in water, and the filtrate evaporated (Gmelin), or by dissolving platinous chloride in cyanide of potassium.[1] The other salts can be obtained by double decomposition.

Platinocyanic Acid, $H_2Pt(CN)_4$, is obtained by decomposing the copper or mercury salt with sulphuretted hydrogen,[2] or by decomposing the barium salt with dilute sulphuric acid.[3] After evaporating to dryness, the residue is treated with a mixture of alcohol and ether, and the ethereal solution allowed to evaporate spontaneously, when fine cinnabar-red prisms, exhibiting a splendid blue colour by reflected light, are obtained. These have the composition $H_2Pt(CN)_4 + 5H_2O$. Sometimes yellowish-green crystals, having a copper-red or golden lustre, are obtained, which contain more water. When heated to 100° they become yellow, and decompose at temperatures above 140°. They are deliquescent, yielding a colourless solution in alcohol; the aqueous solution decomposes carbonates with evolution of carbon dioxide.

Potassium Platinocyanide, $K_2Pt(CN)_4 + 12H_2O$, is obtained by dissolving ammonium platinic-chloride together with caustic potash in a boiling concentrated solution of potassium cyanide. The liquid is boiled until no further evolution of ammonia takes place, when the salt crystallizes out.[4] This is

[1] Knop, *Ann. Chem. Pharm.* xliii. 111.
[2] Quadrat, *ibid.* lxiii. 164; lxv. 249; lxx. 300.
[3] Weselsky, *Journ. Pract. Chem.* lxix. 276.
[4] Martius, *Ann. Chem. Pharm.* cxvii. 357.

also formed when spongy platinum is boiled with solution of cyanide of potassium, or when a mixture of the two bodies is heated at a temperature of from 500° to 600° in steam (Deville and Debray):

$$4KCN + Pt + 2H_2O = K_2Pt(CN)_4 + 2KOH + H_2.$$

It forms long yellow rhombic prisms, exhibiting a blue metallic lustre by reflected light, and being very readily soluble in water. If the hot solution be saturated with chlorine, or boiled with aqua-regia, colourless prisms of potassium chloroplatinocyanide, $K_2Pt(CN)_4Cl_2 + 2H_2O$, are obtained on evaporation. If this solution be mixed in the right proportion with potassium platinocyanide a double salt is obtained of the composition $5K_2Pt(CN) + K_2Pt(CN)_4Cl_2 + 21H_2O$, crystallizing in magnificent green prisms which exhibit a copper-red lustre by reflected light and are soluble in water. This salt, which is also formed when potassium platinocyanide is treated with a moderate quantity of chlorine, was at one time believed to be a platinicyanide corresponding to potassium ferricyanide, as the presence of chlorine in it had been overlooked, and because in alkaline solution it acts as an oxidising agent, and potassium hypochlorite being formed:

$$5K_2Pt(CN)_4 + K_2Pt(CN)_4Cl_2 + 2KOH = 6K_2Pt(CN)_4 + KOCl + KCl + H_2O.$$

Its true composition was first pointed out by Hadow.[1]

Barium Platinocyanide, $BaPt(CN)_4 + 4H_2O$, was first obtained by passing hydrocyanic acid into water containing platinous chloride and barium carbonate in suspension.[2] It can also be easily obtained by decomposing the copper salt by baryta-water. It forms large rhombic crystals which exhibit a green colour in the direction of the primary axis, whilst at right angles to this direction they appear of a sulphur-yellow colour.

Magnesium Platinocyanide, $2MgPt(CN)_4 + 7H_2O$, is obtained by decomposing the barium salt with magnesium sulphate, and is one of the most beautiful salts of this group. It forms large square-based red prisms, the sides of which viewed by reflected light have a beetle-green lustre, whilst the end faces reflect blue or purple light. It crystallizes from alcohol with six molecules of water in four-sided lemon-yellow tables, having a blue reflection,

[1] *Quart. Journ. Chem. Soc.* xiii. 106.
[2] Weselsky, *Journ. Pract. Chem.* lxix. 276.

and often exhibiting all shades of colour of red, blue, and green.

Many other platinocyanides besides these are known, of which several are remarkable for their splendid play of colours. Some, such as the green copper salt, are insoluble powders obtained as precipitates by double decomposition. A very characteristic reaction for the platinocyanides is that on addition of a mercurous or a mercuric salt to their solution a white precipitate is first thrown down, but on addition of more mercurous salt this becomes of a smalt-blue colour.

PLATINOTHIOCYANATES.

629 *Potassium Platinothiocyanate,* $K_2Pt(SCN)_4$, is obtained by dissolving platinum dichloride in a solution of potassium thiocyanate, or better by dissolving equal parts of potassium platinochloride and potassium thiocyanate in the smallest quantity of water, when the mixture becomes warm, and on cooling the salt separates out in red microscopic prisms. When the corresponding barium salt is decomposed by dilute sulphuric acid, the free acid is obtained in solution, but this undergoes rapid decomposition.[1]

PLATINITHIOCYANATES.

630 *Platinithiocyanic Acid,* $H_2Pt(SCN)_6$. On decomposing the lead salt with dilute sulphuric acid, a thick dark-red very acid liquid is obtained, which decomposes carbonates, and dissolves zinc with evolution of hydrogen. On evaporation in a vacuum an indistinct crystalline mass remains behind.

Potassium Platinithiocyanate, $K_2Pt(SCN)_6$, is obtained by adding potassium thiocyanate solution, not in excess, to a solution of potassium platinichloride, and heating to boiling. The filtered solution on cooling deposits large six-sided prisms or tables having a carmine-red colour and possessing a very disagreeable taste. They dissolve in water forming such a deep-red solution that one drop of the concentrated liquid imparts a distinct colour to 100,000 parts of water. When the concentrated solution is boiled with ammonium sulphate a very similar

[1] Buckton, *Quart. Journ. Chem. Soc.* vii. 22.

ammonium platinithiocyanate is formed. The platinithiocyanates of the alkali-metals are soluble in water and crystallizable; those of the heavy metals are insoluble and have a yellowish- or blackish-red colour (Buckton).

PLATINUM AND THE ELEMENTS OF THE SULPHUR GROUP.

631 *Platinum Monosulphide*, PtS, is formed when platinum sponge is heated with sulphur in a vacuous glass tube, or when platinous chloride is fused with carbonate of soda and sulphur, and the mass extracted with water. It forms a green powder or a mass of glistening needles. When heated in the air it decomposes, leaving a residue of platinum, and when ignited in hydrogen it yields sulphuretted hydrogen and spongy platinum.

Platinum Disulphide, PtS_2, is formed as a steel-grey powder by heating ammonium platinic-chloride with sulphur to a dark-red heat. When sulphuretted hydrogen is passed through a solution of a platinic salt a black precipitate of sulphide is first formed, but this by further action of the gas becomes light-brown, from formation of hydrogen platinum sulphide, a compound which on exposure to the air again gives up sulphuretted hydrogen.

Platinum disulphide combines with basic sulphides and therefore dissolves in the sulphides of the alkali-metals.

Potassium Platinothioplatinate, $K_2Pt_4S_6 = K_2S + 3PtS + PtS_2$, is obtained by fusing together platinum sponge, potash, and sulphur, and lixiviating the mass with water. It then deposits in the form of hard six-sided tables, which on heating in the air burn like tinder. Dilute sulphuric acid converts it into $H_2Pt_4S_6$, and this on exposure to air oxidises to *platinum sesquisulphide*, Pt_2S_3, forming a steel-grey crystalline powder.

Di-sodium Platinothioplatinate, $Na_4Pt_3S_6 = 2Na_2S + 2PtS + PtS_2$, is obtained in a similar way to the preceding compound, and forms pale copper-red thin crystalline needles which are converted in contact with hydrochloric acid, without alteration of form, into a reddish-brown compound, $H_4Pt_3S_6$, which oxidizes extremely quickly in the air with formation of the sesquisulphide.[1]

[1] Schneider, *Pogg. Ann.* cxxxviii. 604.

Spongy platinum unites with selenium with incandescence when these substances are heated together, with formation of a grey infusible powder, which, when heated before the blowpipe, loses the whole of its selenium.

PLATINUM AND THE ELEMENTS OF THE PHOSPHORUS GROUP.

These two elements fuse together readily. If finely divided platinum be heated in vapour of phosphorus it burns with evolution of light to form *platinum diphosphide*, PtP_2, which is a bright metallic lustrous mass, not attacked by hydrochloric acid, but easily dissolved by ammonia (Schrötter).

Spongy platinum and arsenic unite with incandescence. The brittle alloy, $PtAs_2$, loses the whole of its arsenic on ignition. Platinum also forms brittle alloys with antimony, bismuth, and vanadium.

Detection and Estimation of Platinum.

632 If a platinum compound be heated on a carbonized match in the gas-flame a grey spongy mass is obtained soluble only in aqua-regia. The concentrated solution yields with potassium chloride and sal-ammoniac the well-known and characteristic precipitates. Sulphuretted hydrogen throws down from solutions of a platinum salt, slowly in the cold but more quickly on heating, the brown disulphide which is soluble in an excess of yellow sulphide of ammonium. A solution of tin dichloride colours platinum chloride solutions dark-brown, inasmuch as platinous chloride is formed.

In the general separation of the metals platinum and gold are obtained together with arsenic, antimony, and tin. Their presence is indicated by the brown colour of the precipitate produced by hydrochloric acid in the solution in sulphide of ammonium. In this case the precipitate is fused with carbonate of soda and nitre, the fused mass lixiviated with water, and the residue, which may contain the gold and platinum together with tin dioxide and sodium antimonate, is treated with zinc and hydrochloric acid when the latter two compounds are reduced to metals. The mass is first boiled with hydrochloric acid to remove the tin, and next with nitric acid and a little

tartaric acid to dissolve the antimony; the residue is then treated with aqua-regia, the solution concentrated and evaporated to dryness on a water-bath with an excess of sal-ammoniac, and alcohol added to dissolve the gold chloride. From the alcoholic solution the gold may be readily precipitated with ferrous sulphate. The portion insoluble in alcohol may contain ammonium platinic-chloride, and this on ignition will leave a residue of spongy platinum.

The *quantitative estimation* of platinum always takes place as metal, obtained by ignition of ammonium platinic-chloride, or by heating potassium platinic-chloride in a current of hydrogen and lixiviating the residue with water, or sometimes also by ignition of the sulphide.

The atomic weight of platinum was determined by Berzelius[1] by analysis of the potassium double chloride; the mean number obtained by him was 196·7, whereas Andrews,[2] who employed the same method, found the atomic weight to be 197·4.

PALLADIUM, Pd = 106·2.

633 In April, 1803, a printed notice[3] came into the hands of Mr. Chenevix, to the effect that a new metal, called Palladium, was to be sold at Mr. Forster's, of Gerrard Street, Soho. Chenevix,[4] believing that this was simply a fraud, bought the whole stock, and after investigating the question he came to the conclusion that the substance was not a new metal, but that it was a platinum amalgam of peculiar properties. Soon after the communication of Chenevix's paper to the Royal Society (May 13, 1803,) an advertisement appeared in which a handsome reward was offered to any one who should prepare even a grain of this substance, either according to Chenevix's plan, or by any other

[1] *Lehrbuch, 5te Aufl.* iii. 1212. [2] *Chem. Gaz.* 1852, 379.

[3] "Palladium, or new silver, has these properties amongst others that show it to be a new noble metal:—1. It dissolves in pure spirit of nitre, and makes a dark-red solution. 2. Green vitriol throws it down in the state of a regulus from this solution, as it always does gold from aqua-regia. 3. If you evaporate the solution you get a red calx that dissolves in spirit of salt or other acids. 4. It is thrown down by quicksilver, and by all the metals but gold, platinum, and silver. 5. Its specific gravity by hammering was only 11·3; but by flattening as much as 11·8. 6. In a common fire the face of it tarnishes a little and turns blue, but comes bright again, like other noble metals, on being stronger heated. 7. The greatest heat of a blacksmith's fire would hardly melt it; 8. But, if you touch it while hot with a small bit of sulphur, it runs as easily as zinc."

[4] *Phil. Trans.* 1803, 290.

method. No one succeeded in obtaining the reward, although several German chemists endeavoured to prepare the new substance. In 1804 Wollaston[1] declared that he was the discoverer of palladium, having taken this name from that of a new planet, Pallas, discovered by Olbers in 1802. At the same time he described the process which he adopted in order to obtain the new metal from platinum ore.

Palladium occurs in a tolerably pure state with Brazilian platinum ore, as well as together with gold, at Tilkerode, in the Harz. It is also contained in most platinum ores, and is found in many places in South America alloyed with gold.

In order to separate it from other platinum metals, use is made of the fact that in neutral solutions mercuric cyanide throws down an insoluble precipitate of palladium dicyanide. Another process is to add potassium iodide to a solution of palladium dichloride, when palladium di-iodide separates out as a black insoluble precipitate. This last reaction has been employed by Bunsen, to prepare pure palladium from the platinum residues from the St. Petersburg mint, which consist of a mixture of all the other platinum metals.[2]

Pure palladium is more readily prepared from commercial palladium, which is obtained, together with the other platinum metals, in the manufactories in which platinum is worked up. Philipp[3] and Guyard[4] have described methods for the working of the platinum metals on the large scale.

In order to purify the commercial palladium the above reactions may be used, or else ammonia may be added to a solution as nearly free as possible from acid, until the precipitate which forms re-dissolves. Hydrochloric acid gas is then passed into the solution, when yellow palladioammonium chloride is thrown down, copper and iron remaining in solution. The washed precipitate leaves after ignition a residue of spongy palladium. The metal is obtained in the same condition by the ignition of the cyanide. Of all the platinum metals palladium has the lowest melting-point, fusing about as readily as wrought-iron, and the fused metal spits like silver on cooling. Palladium has a colour resembling that of platinum, and a specific gravity of 11·4 at 22°5 (Deville and Debray). At the melting-point of iridium in the oxyhydrogen flame palladium begins to boil violently, undergoing partial oxidation, and

[1] *Phil. Trans.* 1804, 428; 1805, 316.
[2] *Phil. Mag.* [4], xxxvi. 253.
[3] *Dingl. Polyt. Journ.* ccxx. 95.
[4] *Compt. Rend.* lvi. 1177.

emitting green vapours, which condense to a brown sublimate consisting of a mixture of oxide and metal.

Palladium is dimorphous. The native metal occurs in the Brazils in the form of sand or rounded grains, amongst which small regular octohedrons are sometimes found. Native palladium usually contains small quantities of both platinum and iridium, and has a specific gravity varying from 11·3 to 11·8. The palladium found in the Harz occurs in small hexagonal tables, together with gold and lead selenide, and hence this latter body was first considered to be palladium selenide. Owing to the difference of crystalline form this variety has been termed by Dana [1] *Allopalladium.*

When palladium is heated to dark redness it assumes a violet or blue colour, but at higher temperatures it regains its metallic lustre, and this remains even when the metal is quickly cooled by plunging into water. Palladium dissolves readily in hot nitric acid, especially when this contains nitrous acid, or when the metal is alloyed with either copper or silver. Spongy palladium also dissolves in hydrochloric acid in contact with the air, and the compact metal likewise dissolves in this acid if chlorine be passed into the liquid. It is likewise attacked by boiling concentrated sulphuric acid, and by fused bisulphate of potash. When warm palladium foil is brought into an electrolytic mixture of hydrogen and oxygen, or other explosive gaseous mixture, combination takes place without explosion (Coquillon),[2] and when the metal is brought into the flame of alcohol or coal-gas it becomes covered with a thick film of soot. When palladium sponge is placed in a current of ethylene this gas is decomposed with separation of carbon, and this occurs at a temperature at which the gas alone does not undergo any alteration.[3]

Palladium has not been employed very largely in the arts. For certain special purposes, however, it is useful; thus on account of its unalterability in the air, and owing to its bright silver-white colour, it has been employed for the preparation of graduated surfaces for astronomical instruments. It is likewise used for coating silver goods, as palladium does not lose its fine white colour on exposure to sulphuretted hydrogen, and hence it has also been much employed by dentists as a substitute for gold.

[1] *Mineralogy*, 5 ed. p. 12. [2] *Compt. Rend.* lxxxiii. 709.
[3] Wöhler, *Liebig's Ann.* clxxxiv. 128.

PALLADIUM AND HYDROGEN.

634 *Palladium Hydride*, Pd_2H_4. This compound, discovered by Graham,[1] has been already described in Vol. I., p. 105. It is formed by passing hydrogen over metallic palladium heated to redness, or by bringing the metal into contact with nascent hydrogen. The formation of this compound is accompanied by evolution of heat.[2] It possesses all the properties of a metal; it has a metallic lustre, is tough, conducts electricity, and is distinctly magnetic. The specific gravity of palladium hydrogenide is 11·06, and it possesses the power of absorbing varying quantities of hydrogen.[3] On exposure to air this compound sometimes becomes heated from absorption of oxygen and formation of water. As a rule, however, it does not undergo alteration either in the air or in a vacuum, at the ordinary temperature, although it gives up its hydrogen on ignition. The specific gravity of palladium hydride is less than that of the metal, hence an expansion of the metal must occur in the formation of the compound. This expansion can be shown in several ways. One of the most striking is to fix two palladium wires horizontally through the edges of a thin electrolytic trough with parallel glass sides. The trough is then filled with acidulated water, placed in the focus of the oxyhydrogen or electric light, and the image of the wires thrown on the screen. A current of electricity, from two or three Grove's elements, is now allowed to pass through the cell, when a singular bending of the palladium wire from which the hydrogen is evolved is noticed. If the current be reversed this wire first returns to its original horizontal position, and then bends to the opposite side, whilst the other wire is deflected in the former direction. The explanation of this double bending being that first one side, and then the other side of the wire becomes saturated with, or loses the hydrogen.[4]

If one side of a piece of palladium foil be saturated electrolytically with hydrogen, then taken out of the liquid, washed and dried, and afterwards ignited, it becomes so bent that it has almost the appearance of having been rolled up into a coil.

[1] *Phil. Mag.* [4], xxxii. 516. [2] Favre, *Comptes Rendus*, lxxi. 214.
[3] Troost and Hautefeuille, *Comptes Rendus.* lxxviii. 686.
[4] Poggendorff, *Ber. Deutsch. Chem. Ges.* ii. 74; also Dewar, *Phil. Mag.* [4], xlvii. 334.

The arrangement shown in Fig. 172 is that proposed by Wöhler[1] for exhibiting the decomposition of palladium hydride by heat and the reabsorption of the hydrogen on cooling.

The U-tube (*a*) dipping in boiling-water contains the spongy-palladium, over which a current of hydrogen is passed for half an hour from the cylindrical generator on the right of the figure. The water-bath is then removed and the tube allowed to cool in

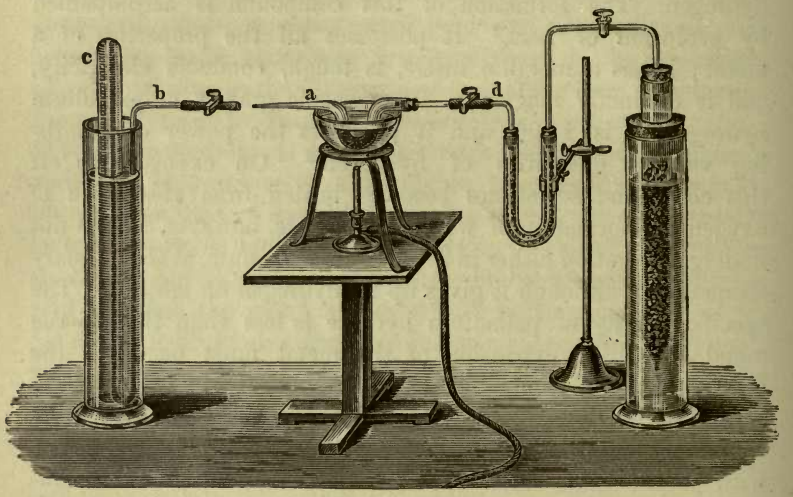


Fig. 172.

the current of hydrogen. The stop-cock (*d*) is now shut, and the tube (*a*) placed in communication with the tube (*b*). This latter dips in the cylinder and is bent up at the lower end into the tube (*c*). The tube (*a*) is next heated with a flame, when the cylinder soon becomes filled with hydrogen, and on allowing the spongy metal to cool, a rapid absorption of the hydrogen occurs. The experiment can, of course, be repeated as often as is required.

PALLADIUM AND OXYGEN.

635 *Palladium Hemioxide*, Pd_2O, is a black powder, giving rise, on ignition, to the following compound. When ignited to dull redness in hydrogen it becomes strongly heated, aqueous vapour

[1] *Ann. Chem.* clxxxiv. 128.

being evolved with almost explosive violence. Acids decompose it into the metal and a palladium salt.[1]

Palladium Monoxide, PdO, is formed by heating the nitrate or other palladium salt mixed with potassium carbonate. It is an amber-coloured mass, having a metallic lustre, and yielding a black powder. On strong ignition it yields the metal, and is reduced by hydrogen at the ordinary temperature with evolution of light and heat. If a palladious salt be precipitated with sodium carbonate a dark-brown hydroxide, readily soluble in acids, is thrown down, whilst the anhydrous oxide dissolves only after long boiling.

Palladium Dioxide, PdO_2, is obtained as a black powder by boiling palladioammonium chloride with caustic soda. On heating this is converted into the monoxide. If the above double salt be dissolved in cold caustic soda, a yellowish-brown hydroxide separates out, on standing, in the form of a gelatinous precipitate readily soluble in acids.

PALLADIOUS SALTS.

636 These salts possess a green, red, or brown colour, and have an astringent, but not a metallic taste.

Palladious Chloride, $PdCl_2$, is obtained by heating palladious sulphide, PdS, in dry chlorine, when it is obtained partly as a rose-red sublimate and partly in the form of garnet-red crystals, which dissolve slowly but completely in water. It is prepared in solution by the simultaneous action of chlorine and hydrochloric acid on the metal. On evaporation over caustic lime brown-red crystals having the composition $PdCl_2 + 2H_2O$, are deposited. These lose water when gently heated, the anhydrous chloride remaining as a brownish-black mass which melts easily without decomposition. At a red-heat it fuses and loses half of its chlorine, forming the monochloride, Pd_2Cl_2, which, on cooling, solidifies to a reddish-brown crystalline mass yielding a light-red powder which is very deliquescent. The aqueous solution partially decomposes with separation of metal.

Palladious chloride forms double chlorides with other chlorides; thus:

Potassium Palladiochloride, K_2PdCl_4, is obtained by dissolving the metal in hydrochloric acid to which nitre has been added, or

[1] Kane, *Phil. Trans.* 1842, i. 276.

by evaporating the solution of the metal in aqua-regia until the excess of acid has been driven off, and then adding chloride of potassium. It may also be prepared by the ignition of potassium palladic-chloride. It is easily soluble in water, less so in alcohol, and crystallizes in four-sided prisms, which when viewed in the direction of the primary axis have a red, but in other directions exhibit a light-green colour.

Ammonium Palladiochloride, $(NH_4)_2PdCl_4$, is obtained by evaporating a solution of the chloride with sal-ammoniac. It forms either bronze-yellow prisms exhibiting a play of different colours, or needles, and dissolves in water with a dark-red colour.

Palladious Iodide, PdI_2, is obtained by precipitating the chloride with potassium iodide as a black flocculent precipitate which when dried in the air forms a deliquescent mass exhibiting a conchoidal fracture. It dissolves slowly in hydriodic acid and readily in a solution of potassium iodide, imparting to this a wine-red colour. When heated to 100° it begins to give off iodine and decomposes completely at temperatures between 330° and 360°. The solution in potassium iodide yields on evaporation blackish-green deliquescent cubes.

Palladious Sulphate, $PdSO_4 + H_2O$, is obtained by dissolving the hydroxide in sulphuric acid, or by dissolving the metal in the same solvent with the addition of nitric acid. It forms indistinct olive-green deliquescent crystals which are decomposed by water with formation of a basic salt, $PdSO_4 + 7Pd(OH)_2$, as a brown insoluble powder.

Sodium Palladiosulphite, $Na_6Pd(SO_3)_4 + 2H_2O$, is obtained as a white crystalline precipitate by adding caustic soda to a solution of the chloride which has been saturated with sulphur dioxide.

Palladious Nitrate, $Pd(NO_3)_2$, is formed by dissolving the metal or the oxide in nitric acid. It crystallizes in long brownish-yellow rhombic prisms which probably contain water of crystallisation, and are very deliquescent. A brown powder of $Pd(NO_3)_2 + 3Pd(OH)_2$, is formed on the addition of water to the solution.

Potassium Palladionitrite, $K_2Pd(NO_2)_4$, is obtained on addition of potassium nitrite to a hot solution of potassium palladio-chloride.

PALLADIC SALTS.

637 Although the dioxide readily dissolves in acids, none of its simple salts are known in the pure state, these readily changing into palladious salts.

Palladic Chloride, $PdCl_4$, is obtained by dissolving the metal in concentrated aqua-regia. The brown solution doubtless contains *chloropalladic acid*, H_2PdCl_6, corresponding to chloroplatinic acid.

Potassium Palladichloride, K_2PdCl_6, is obtained by adding potassium chloride to a solution of the metal in an excess of aqua-regia, and gently evaporating. It is also prepared by precipitating a solution of palladium chloride, saturated with chlorine, with an excess of potassium chloride. It forms cinnabar-red or brownish-red octohedrons showing the faces of the cube. These dissolve in hot dilute hydrochloric acid without decomposition, but are not soluble in water containing the chlorides of the alkali metals, or in alcohol.

Ammonium Palladichloride, $(NH_4)_2PdCl_6$, is a bright-red crystalline powder consisting of microscopic octohedrons. It is obtained by precipitating a solution of the chloride, saturated with chlorine, by sal-ammoniac. On treating the solution with an excess of ammonia a violent evolution of nitrogen takes place, ammonium palladiochloride being formed:

$$3(NH_4)_2PdCl_6 + 2NH_3 = 3(NH_4)_2PdCl_4 + 6HCl + N_2.$$

AMMONIACAL PALLADIUM COMPOUNDS.

638 These have been chiefly investigated by Hugo Müller,[1] and are formed by the action of ammonia on palladious salts. Of these, two bases exist to which he gave the names palladamine and palladdiamine. These are, however, now known respectively as palladammonium hydroxide, and palladdiammonium hydroxide.

Palladammonium Hydroxide, $Pd(NH_3)_2(OH)_2$, is obtained by the decomposition of the sulphate with baryta-water, or of the chloride with oxide of silver and water. The yellow solu-

[1] *Ann. Chem. Pharm.* lxxxvi. 341.

tion thus obtained when dried over sulphuric acid yields a crystalline ochre-yellow mass. The solution has a strongly alkaline reaction, readily absorbs carbon dioxide, and has a bitter taste, producing insensibility on that portion of the tongue which has been in contact with it. It precipitates the salts of copper and silver and decomposes ammonium salts on boiling.

Palladammonium Chloride, $Pd(NH_3)_2Cl_2$, is obtained by the addition of an excess of ammonia to palladious chloride and either evaporating, or, better, precipitating the salt by means of hydrochloric acid. It forms fine yellow needles which consist of glistening octohedrons placed one upon the other, and it is almost insoluble in water.

Palladammonium Sulphate, $Pd(NH_3)_2SO_4$, is obtained by decomposing the chloride with silver sulphate. It is tolerably soluble in water and crystallizes in small orange-yellow octohedrons.

Palladdiammonium Hydroxide, $Pd(NH_3)_4(OH)_2$, is obtained by the decomposition of the sulphate with baryta water. It is a colourless crystalline mass, the aqueous solution of which has a strong alkaline reaction, precipitates the salts of copper, iron, cobalt, nickel, and aluminium, but not those of silver, and decomposes ammoniacal salts.

Palladdiammonium Chloride, $Pd(NH_3)_4Cl_2$, is formed by the repeated evaporation of palladious chloride with ammonia. It crystallizes in large, colourless, four-sided, monoclinic prisms, and is easily soluble in water.

Besides these there are known several other palladammonium salts which all crystallize well.

Palladious Cyanide, $Pd(CN)_2$, is obtained as a pale-yellow precipitate on addition of mercuric cyanide solution to a solution of a palladious salt, which must contain no free acid and should not be too dilute. On solution in potassium cyanide and evaporation, transparent thin rhombic prisms of *potassium palladiocyanide*, $K_2Pd(CN)_4 + 3H_2O$, or small tables of $K_2Pd(CN)_4 + H_2O$ are obtained. The cyanide is also soluble in acids and in ammonia, and the latter solution yields *palladosammonium cyanide*, $Pd(NH_3)_2(CN)_2$, in needles or in crystalline scales possessing a pearly lustre.

PALLADIUM AND SULPHUR.

639 *Palladium Hemisulphide,* Pd_2S, is obtained by fusing ammonium palladiochloride with carbonate of soda, sulphur, and sal-ammoniac. A green molten mass is thus obtained which crystallizes on cooling and exhibits a metallic fracture. It is only slowly attacked by aqua-regia.

Palladium Monosulphide, PdS, is formed with incandescence by heating the metal in the vapour of sulphur. It is a bluish-white hard metallic lustrous mass with a laminated fracture, which only oxidizes slowly in the air. It is also obtained as a black precipitate by passing sulphuretted hydrogen through a solution of a palladious salt.

Palladium Disulphide, PdS_2. When the foregoing compound is fused with carbonate of soda and sulphur, *sodium thiopalladate,* Na_2PdS_3, is formed. This crystallizes in reddish-brown needles, having a slightly metallic lustre. It is decomposed by hydrochloric acid with formation of the disulphide, which is a crystalline dark-brown powder easily soluble in aqua-regia. When heated in carbon dioxide it is first converted into the monosulphide, and at a higher temperature into the hemisulphide.

Detection and Estimation of Palladium.

640 The two most characteristic reactions of palladium are (1) the precipitation of its hydrochloric acid solution by cyanide of potassium, the yellowish-white cyanide of palladium being thrown down, soluble in both hydrochloric acid and ammonia; and (2) the production of a black precipitate of palladious iodide, insoluble in hydrochloric acid, when potassium iodide is added to a palladium solution. By these reactions it may be separated from all metals, with the exception of copper, and this may be previously removed, according to Wöhler, by precipitation as cuprous thiocyanate after saturation with sulphur dioxide.

Palladium is determined *quantitatively* as the metal, usually obtained by the ignition of the cyanide.

The atomic weight of palladium was determined by Berzelius by the analysis of potassium palladiochloride, K_2PdCl_4.

[1] *Pogg. Ann.* xiii. 435.

RHODIUM. Rh = 104·1.

641 When Wollaston[1] in 1804 first acknowledged that he was the discoverer of palladium, he likewise intimated that he had found another new metal in platinum ore, to which he gave the name of rhodium, because the solutions of this salt possess a rose-red colour (*ῥόδον*, a rose). After Wollaston's time the metal and its compounds were investigated by Berzelius and Claus. In addition to its occurrence in platinum ore, rhodium has been found, according to Del Rio, alloyed with gold as rhodium-gold.

In order to prepare rhodium, the solution is employed from which ammonium platinic-chloride has been precipitated. The metals still in solution are then precipitated by metallic iron, and, according to the process of Deville and Debray, the metallic precipitate is fused with one part of lead and two parts of litharge. A regulus is thus obtained, from which the lead, copper, and palladium may be dissolved out by the action of dilute nitric acid. The insoluble metallic powder is then well mixed with five parts of barium dioxide and heated to redness for two hours, the solid mass being lixiviated with water, and the residue boiled with aqua-regia in order to volatilize the osmium tetroxide, this latter being condensed. The excess of barium is precipitated from the solution by sulphuric acid. The filtrate evaporated at 100° with an excess of sal-ammoniac, and the residue washed with sal-ammoniac solution as long as the wash-water has a rose-red colour. The filtrate is then evaporated with an excess of nitric acid in order to decompose the sal-ammoniac, and the residual mass heated to redness with from three to four parts of sulphur. It is then rapidly boiled out with aqua-regia and sulphuric acid, and by this treatment nearly pure rhodium remains behind. In order further to purify this, it is fused with from three to four parts of zinc, and the alloy treated with strong hydrochloric acid, when the compound $RhZn_2$ remains behind. This is dissolved in aqua-regia and evaporated with an excess of ammonia. Rhodammonium chloride, $Rh_2(NH_3)_{10}Cl_2$, separates out, and this is then purified by recrystallization, and ignited in a carbon crucible with some sulphur, and lastly, in order to remove from it the last traces of silicon and osmium, fused in the oxyhydrogen furnace.

[1] *Phil. Trans.* 1804, 419.

Another method of preparing the pure metal is that described by Bunsen,[1] for the particulars of which his memoir on the subject must be consulted. He obtained from one kilogram of the platinum residues from the St. Petersburg mint 33·2 grams of pure rhodium sodium sulphate, $Na_6Rh_2(SO_4)_6$.

Properties. Rhodium possesses the colour and lustre of aluminium and has a specific gravity of 12·1. It fuses with greater difficulty than platinum, and spits on cooling, the surface becoming coloured blue from oxidation. When a solution of one of its salts is heated with sodium formate, the metal is precipitated in the form of a fine black powder, possessing the property of decomposing formic acid, CH_2O_2, with evolution of heat, into hydrogen and carbon dioxide. After a time the action becomes weaker, but the powder then simply requires to be washed with water and dried in the air to enable it to regain its original activity. At a somewhat higher temperature, and in presence of caustic potash, it also decomposes alcohol, C_2H_6O, with evolution of hydrogen and formation of potassium acetate, $C_2H_3O_2K$. It does not lose this power at a temperature at which glass begins to soften (Deville and Debray). Pure rhodium, as well as that which contains gold and platinum, is almost insoluble in acids. If, however, it be alloyed with bismuth, zinc, lead, or copper, it dissolves in aqua-regia. Alloys of much platinum and little rhodium dissolve also in aqua-regia, but if the rhodium be present in larger quantity much remains undissolved. Rhodium can, however, be brought into solution by repeated ignition with fused bisulphate of potash, as well as with phosphoric acid or acid phosphates. Of all the platinum metals rhodium is the most easily attacked by chlorine.

RHODIUM AND OXYGEN.

642 Rhodium forms three oxides, having the formulæ RhO, Rh_2O_3, and RhO_2.

Rhodium Monoxide, RhO, is obtained by heating the sesquihydroxide, $Rh_2(OH)_6$, or by the cupellation of an alloy of rhodium and lead. It is a grey powder with metallic appearance, which is not attacked by acids, and when heated in hydrogen it is reduced with evolution of light.

Rhodium Sesquioxide, Rh_2O_3, is obtained as a grey iridescent

[1] *Phil. Mag.* [4], xxxvi. 253.

spongy mass by heating the nitrate. It is also formed as a crystalline mass when sodium rhodiochloride is heated in oxygen. It is perfectly insoluble in acids.

Rhodium Sesquihydroxide, $Rh_2(OH)_6$, is a black gelatinous precipitate, obtained by heating a solution of sodium rhodiochloride with caustic potash. On drying it forms a heavy dark-brown metallic lustrous mass having a conchoidal fracture. It is scarcely attacked by acids, hydrochloric acid dissolving it but very slightly.

If a solution of the sodium double salt be treated with an excess of potash in the cold it becomes opaque, and on long standing deposits thin lemon-yellow crystals of the hydrate $Rh_2(OH)_6 + 2H_2O$, which dissolve readily in acids, and, when moist, in caustic potash.

Rhodium Dioxide, RhO_2, is obtained by repeated fusion of the metal with caustic potash and saltpetre. The sesquioxide is first formed, and this undergoes further oxidation. It closely resembles the sesquioxide; it is attacked neither by alkalis nor by acids, and is reduced by hydrogen only at a high temperature.

Rhodium Tetrahydroxide, $Rh(OH)_4$. When chlorine is passed into the alkaline solution of the sesquihydroxide for a long time and caustic potash occasionally added, this compound separates out as a green powder, the liquid becoming of a blue or violet tint. The green powder dissolves in hydrochloric acid, yielding a blue solution, and this colour gradually changes to dark-red, chlorine being evolved. The violet-blue solution probably contains the potassium salt of a rhodic acid, which latter separates out after some time as a blue powder, gas being simultaneously evolved. On drying, it is converted into the tetrahydroxide.

RHODIUM SALTS.

643 The rhodium salts are derived from the sesquioxide. They possess either a dark-red or a yellow colour, and have a bitter but not astringent taste.

Rhodium Chloride, Rh_2Cl_6, is obtained by the continued ignition of the finely-divided metal in chlorine, and also by heating one of the alkaline double salts with sulphuric acid, and pouring the cooled mixture into water; a rose-red powder of insoluble

rhodium chloride remains behind. When the yellow hydroxide is dissolved in hydrochloric acid, a yellow solution is obtained possessing an astringent taste. On evaporation this becomes rose-red, and then possesses the peculiar bitter taste characteristic of all rhodium salts. A dark-red amorphous mass of the hydrated chloride is obtained when this solution is evaporated. It is then deliquescent, and on heating yields the insoluble anhydrous chloride.

Potassium Rhodiochloride, $K_4Rh_2Cl_{10} + 2H_2O$, is obtained by heating a mixture of rhodium and potassium chloride in a current of chlorine, or by the addition of potassium chloride to a solution of rhodium chloride. It forms dark-red four-sided rather difficultly soluble prisms. If the yellow hydroxide be dissolved in hydrochloric acid, and a concentrated solution of potassium chloride added, the liquid being then allowed to evaporate spontaneously, dark-red glistening triclinic prisms are obtained of $K_6Rh_2Cl_{12} + 6H_2O$. These are very difficultly soluble, and the solution has a cinnabar-red colour, with a tinge of violet.

Sodium Rhodiochloride, $Na_6Rh_2Cl_{12} + 24H_2O$, is obtained like the last mentioned of the potassium salts, and crystallizes in large cherry-red-coloured triclinic prisms, having an almost black lustre. The crystals gradually effloresce on exposure to moist air, yielding a peach-blossom-coloured powder. A salt containing four atoms of sodium has not yet been obtained.

Ammonium Rhodiochloride, $(NH_4)_6Rh_2Cl_{12} + 3H_2O$, is formed when solutions of rhodium chloride and sal-ammoniac are allowed to evaporate spontaneously in a warm situation. It closely resembles the sodium salt. When its solution is boiled light-red prisms or tables separate out, having the composition $(NH_4)_4Rh_2Cl_{10} + 2H_2O$. These are less soluble in water than the original salt.

Rhodium Sulphate, $Rh_2(SO_4)_3 + 12H_2O$, is obtained by dissolving the yellow hydroxide in sulphuric acid, evaporating, and washing away the excess of acid by alcohol. It is a yellow crystalline mass which possesses a sour astringent taste. It forms double salts with the salts of the alkalis, such as $K_6Rh_2(SO_4)_6$, &c.

Rhodium Sulphite, $Rh_2(SO_3)_3 + 6H_2O$, is obtained by dissolving the yellow hydroxide in sulphurous acid and evaporating. It forms a pale-yellow indistinctly crystalline mass.

Rhodium Nitrate does not crystallize, and, like the chloride, exists in both a red and a yellow modification.

Potassium Rhodionitrite, $K_6Rh_2(NO_2)_{12}$. This is obtained, by heating a solution of the chloride with potassium nitrite, as a reddish-yellow, heavy, slightly soluble, crystalline powder, which dissolves readily in hydrochloric acid.

Sodium Rhodionitrite, $Na_6Rh_2(NO_2)_{12}$, is prepared in a similar way. It is a light-yellow powder, consisting of microscopic octohedrons, and is only slowly decomposed on warming with concentrated hydrochloric acid.

AMMONIACAL RHODIUM COMPOUNDS.

644 These compounds, first described by Claus in 1854, correspond to the ammoniacal compounds of iridium.

Rhodammonium Hydroxide, $Rh_2(NH_3)_{10}(OH)_6$, is obtained by warming rhodammonium chloride with water and silver oxide, and evaporating the solution. It forms a yellowish crystalline mass which possesses a strongly alkaline reaction.

Rhodammonium Chloride, $Rh_2(NH_3)_{10}Cl_6$, is prepared by evaporating a dilute solution of ammonium rhodiochloride with excess of ammonia. It forms small yellow slightly soluble prisms, which dissolve in caustic potash with evolution of ammonia.

Rhodammonium Sulphate, $Rh_2(NH_3)_{10}(SO_4)_3$, is deposited in large yellowish prisms when the base is saturated with sulphuric acid.

Rhodammonium Nitrate, $Rh_2(NH_3)_{10}(NO_3)_6$, forms colourless crystals, and has a faint saline taste.

Rhodammonium Carbonate, $Rh_2(NH_3)_{10}(CO_3)_3 + 3H_2O$, is a white saline mass unalterable in the air and possessing a saline taste and alkaline reaction. It is formed when rhodammonium hydroxide is exposed to an atmosphere of carbon dioxide.

Potassium Rhodicyanide, $K_6Rh_2(C_3N_3)_4$, is obtained in a similar way to the corresponding iridium salt (see p. 447), which it closely resembles, but may be distinguished from it inasmuch as acetic acid produces a pale crimson-red precipitate of rhodium cyanide, $Rh_2(CN)_6$, which dissolves in the cyanides of the alkali-metals, forming the rhodicyanides (Martius).

RHODIUM AND SULPHUR.

Rhodium Monosulphide, RhS. When rhodium is heated in sulphur vapour it takes fire with formation of the sulphide, which is also produced when sulphuretted hydrogen is passed through a solution of a rhodium salt, and the washed precipitate dried by ignition in a current of carbon dioxide. Thus obtained, it forms a bluish-white fused mass having a metallic lustre, which, when heated in the air, leaves a residue of spongy rhodium.

The sulphides of the alkali-metals give a brown precipitate with rhodium salts, which is soluble in potassium sulphide, and probably consists of Rh_2S_3.

Detection and Estimation of Rhodium.

645 Solutions of this metal are precipitated by sulphuretted hydrogen, slowly in the cold, but more quickly when warmed. The brown sulphide is insoluble in ammonium sulphide. When a rhodium compound is heated in hydrogen the metal is obtained; this is insoluble in aqua-regia, but can be obtained in solution when it is fused with acid potassium sulphate; the fused mass on treatment with water yields a red solution. From this the metal is precipitated as a black powder on addition of caustic potash and alcohol. It is also precipitated from acid solution by zinc and other metals.

Rhodium is determined quantitatively as the metal.

The *atomic weight* of rhodium has been determined by Berzelius[1] and Claus.[2]

IRIDIUM. Ir. = 192·7.

646 In 1803 Smithson Tennant investigated the metallic residue which remains when platinum ores are dissolved, and this he believed to contain a new metal. At the same time Descotils, as well as Fourcroy and Vauquelin, examined the same subject, and also came to the conclusion that the solution contained a

[1] *Pogg. Ann.* xiii. 435.
[2] *N. Petersb. Akad. Bull.* ii. 158.

peculiar metal. However, in 1804 Tennant[1] proved that the platinum residues contained two new metals, to one of which he gave the name of iridium, on account of the varying colour of its salts, and to the other the name osmium (*ὀσμή*, a smell), because of the peculiar odour which its volatile oxide possesses.

Iridium is found in the platinum ores in considerable quantity in the form of the alloys platiniridium and osmiridium. The first of these occurs in grains, and often in small cubes with rounded edges; the second usually in flat, irregular grains, and occasionally in hexagonal prisms. The composition of these minerals is shown in the following analyses:

	Platiniridium.		Osmiridium.			
	Urals.	Brazil.	Ural.	New Granada.	California.	Australia.
Iridium . .	76·85	27·79	55·24	57·80	53·50	58·13
Osmium .	—	—	27·23	31·10	43·40	33·46
Platinum .	19·64	55·44	10·08	—	—	—
Rhodium .	—	6·86	1·51	0·63	2·60	3·04
Ruthenium.	—	—	5·85	6·37	0·50	5·22
Palladium .	0·89	—	trace	—	—	—
Iron . . .	—	4·14	trace	0·10	—	—
Copper . .	1·78	3·30	trace	0·06	—	0·15
	99·16	98·02	100·00	100·06	100·00	100·00

647 Many methods have been published for the separation of iridium from the other metals, and for the preparation of its salts in the pure state. A very ready process for obtaining pure iridium has recently been described by G. Matthey.[2]

The problem of the preparation of large quantities of pure iridium is one which has recently engaged the attention of chemists on account of its employment in the preparation of the standard meter-measures which were ordered to be prepared by the Parisian Commission for the International Metrical System. This alloy, consisting of 1 part of pure iridium and 9 of platinum, is extremely hard, as elastic as steel, more difficultly fusible than platinum, perfectly unalterable in the air, and capable of taking an exceedingly beautiful polish.

[1] *Phil. Trans.* 1804, 411. [2] *Proc. Roy. Soc.* 1879.

About the year 1870 Messrs. Johnson, Matthey & Co. prepared a standard-metal bar of the platinum-iridium alloy, and sent it to Paris, where it was subjected to every possible test which could be suggested in competition with the other materials which had been proposed or had at that time been adopted for standard measures. After two years' trial this alloy was pronounced to be the best, and when, in 1872, the International Commission was formed, the employment of this alloy was decided upon, and the above-named firm undertook to prepare in six months all the rules and weights required by the Commission (about fifty of each), of full purity and density. The French section of the Commission, to whom the manufacture of the rules was intrusted, decided that the requisite quantity of pure platinum and of unrefined iridium should be purchased from the above firm of English metallurgists. Accordingly it was supplied with iridium containing about 95 per cent. of the pure metal. This was refined in France under the superintendence of the Commission by Messrs. Deville and Debray, who carried it out in the following way. After ignition with barium nitrate, and treatment of the mass with water, the residue was found to consist of iridium oxide and barium osmate. This was boiled with nitric acid in order to remove the osmium, which volatilised as the tetroxide. The iridium oxide was precipitated from the residual solution by baryta, dissolved in aqua-regia, and then thrown down as the double chloride of iridium and ammonium. This, on ignition, yielded spongy iridium, containing small quantities of platinum, ruthenium, and a little rhodium. The metal was then ignited with potassium nitrate, and the mass treated with water, when potassium ruthenate dissolved. It was lastly fused with lead, the regulus obtained leaving, after treatment with nitric acid and aqua-regia, a residue of pure iridium.

To ensure homogeneity in all the standards it was considered desirable that the whole of the prepared iridium and platinum (250 kilos. = 4 cwt. 3 qrs. 19 lbs. English weight) should be ultimately melted at one fusion, and this operation was, at the request of the members of the International Commission, organised and carried out under the personal superintendence of Mr. George Matthey, whose firm lent the requisite fusing appliances, the general arrangements for it being undertaken and carried out by M. Tresca at the Conservatoire des Arts et

Métiers. The alloy was first melted into small lumps weighing from ten to fifteen kilos., and subsequently the whole of the pieces so prepared were fused together in one large ingot or pig. For this purpose seven melting apparatus were required, and in about one and a half hours the whole mass was fused by employing about thirty-one cubic meters of oxygen and twenty-four cubic meters of coal-gas.[1]

On examination it was, however, found that the metal thus obtained was not of the proper density, and analysis proved that it was impure. The platinum supplied was shown to be pure, and the iridium had been properly refined by MM. Deville and Debray. But it is supposed that by a mistake some ruthenium residues had been unfortunately mixed with the iridium, and thus caused the mischief. M. Deville and some other members of the Commission proposed that the refining processes should be repeated, but their advice was overruled, and M. Deville retired from the Commission. The Commission then decided that the form of the rule should be that shown in section in Fig. 173, and that it should be made by drawing the metal. Messrs. Johnson, Matthey, and Co., on the other hand, suggested that the form of the rule should be that shown in section in Fig. 174, and urged that, under any circumstances, the

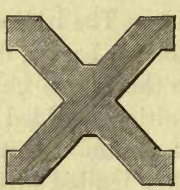


Fig. 173.

Fig. 174.

metal should not be drawn through plates, but *planed* into shape, inasmuch as it is only in this way that mathematical accuracy of shape and complete uniformity of molecular condition can be attained. The result of the undertaking appears to be that after five years of labour and expense not a single rule has been produced in France which can be regarded as perfect either in composition or in form. Some standard rules have, however, been lately ordered from the London firm above referred to, by the French Minister of Agriculture and Commerce, and by the French Minister of War, some of which already furnished have

[1] *Compt. Rendus*, lxxviii. 1502.

been acknowledged as perfect in composition, manufacture, and physical properties. The alloy on analysis gave the following result:

Pt.	Ir.	Rh.	Ru.	Fe.
89·41	10·17	0·17	0·10	0·06

After osmium and ruthenium, iridium is the most difficultly fusible of the platinum metals. It possesses a white lustre, resembling that of polished steel. In the cold it is very brittle, but at a white-heat it is somewhat malleable. It has a specific gravity of 22·38, and is slightly volatile. If the alcoholic solution of the sulphate be exposed to the sunlight the metal is deposited as an extremely fine impalpable black powder, which, when washed with hot-water and dried, acts even more energetically in bringing about the combination of combustible gases than does platinum black. The smallest trace brought on to paper saturated with alcohol produces ignition, the metal at the same time being converted into a grey sponge. Spongy iridium is prepared by igniting the double chloride of iridium and ammonium. This oxidises in the air, and when ignited becomes dense and lustrous, and then absorbs oxygen only slowly, whilst the coherent metal does not do so at all. Iridium black, as well as the coherent metal, when alloyed with much platinum, dissolves in aqua-regia. Pure massive iridium is, however, not attacked. When it is heated with acid potassium sulphate, or in presence of fused alkalis, it is oxidized, and it unites directly with chlorine at a dull red-heat. When the metal is held in the middle of a flame of alcohol it becomes covered with a black moss-like deposit, which has the composition IrC_4, and easily takes fire on exposure to the air. The metal is in this case penetrated throughout its mass with carbon, and becomes of a dark grey colour. The oxides are also converted into the carbide of iridium, with evolution of light and heat, when they are heated in gases or vapours containing carbon.

IRIDIUM AND OXYGEN.

648 *Iridium Sesquioxide*, Ir_2O_3, is formed by the ignition in air or in oxygen of the finely divided metal. A singular property of this oxide is that it begins to decompose again when heated above 800°, and at temperatures somewhat above 1000° it is

completely resolved into oxygen and the metal. Hence the metal is quite unalterable at any higher temperature.

Messrs. Deville and Debray[1] have lately investigated this subject, observing the dissociation into metal and oxygen which the oxide undergoes when heated in a porcelain tube. At a temperature of 1139° the oxide rapidly gives off oxygen, and metallic iridium remains behind in the tube. The tension of dissociation, that is, the tension of the liberated gas, at the several temperatures was found to be as follows:

T°	Tension.
823°	5 mm.
1003°	203 „
1112°	711 „
1139°	745 „

The oxide is also formed when potassium iridichloride is mixed with carbonate of soda and heated to dull redness:

$$2K_2IrCl_6 + 4Na_2CO_3 = Ir_2O_3 + 8NaCl + 4KCl + 4CO_2 + O.$$

The fused mass is washed with water containing sal-ammoniac, and the residue, after ignition to expel the sal-ammoniac, is treated with dilute acid in order to remove the small quantity of alkali. A bluish-black powder is thus obtained which decomposes into the metal and oxygen when heated to the fusing point of silver. In the pure state it imparts to porcelain after firing a fine black colour, and when mixed with zinc oxide it yields a grey tint.

Iridium Sesquihydroxide, $Ir_2(OH)_6$, is obtained by a process similar to that employed for the preparation of the corresponding rhodium compound, which it closely resembles. If a small quantity of caustic potash be added to a solution of the double salt of iridium sesquichloride, and this solution be allowed to stand in a closed bottle, a yellowish-green precipitate of the hydroxide falls down, which readily dissolves in alkalis and oxidizes quickly in the air.

Iridium Dioxide, IrO_2, is a black powder obtained by heating the hydroxide in a current of carbon dioxide. It is insoluble in acids.

Iridium Tetrahydroxide, $Ir(OH)_4$, is formed by the oxidation of the sesquihydroxide in the air, or by precipitating the tetrachloride with an alkali. It is a heavy indigo-blue powder which

[1] *Comptes Rendus*, lxxxvii. 441.

is almost insoluble in dilute sulphuric and nitric acids, but dissolves completely though slowly in hydrochloric acid. On heating the indigo-blue solution it becomes green and then brown.

SALTS OF IRIDIUM.

649 Iridium forms two series of salts corresponding to the hydroxides. Besides these Seubert [1] has recently described another series corresponding to the monoxide. The following double salts were obtained by him in the course of the separation of iridium from rhodium according to Bunsen's method with bisulphite of soda.

The salt, $IrSO_3 + 3Na_2SO_3 + 10H_2O$, is obtained in cream-coloured scaly crystals, whilst another compound having the formula $IrH_2(SO_3)_2 + 3Na_2SO_3 + 4H_2O$ forms broad milky needles, and $IrH_2(SO_3)_2 + 3Na_2SO_3 + 10H_2O$ exists in fine white needles. These salts have an acid reaction, they are almost insoluble in cold water and are decomposed by hot water and acids. When ammonium iridichloride is heated with aqueous sulphurous acid to 70° a liquid is obtained which appears olive-green by reflected, but reddish-brown by transmitted light, and from which a moss-green crystalline powder is deposited. If this be dissolved in water and the solution crystallized ammonium iridiochloride first separates, whilst a crop of orange-red needles of the acid $H_2SO_3.IrCl_2.4NH_4Cl$ are afterwards deposited. This acid forms red crystalline salts with alkalis, such as $K_2SO_3.IrCl_2.2NH_4Cl + 4H_2O$ and $(NH_4)_2SO_3.IrCl_2.2NH_4Cl + 4H_2O$, crystallizing respectively in small scales and in rhombic tablets.

IRIDIOUS SALTS.

650 *Iridious Chloride*, Ir_2Cl_6, is prepared by heating one of its double salts with sulphuric acid. If the mass be then thrown into water the chloride separates out as a light olive-green precipitate insoluble in acids and in alkalis. It is obtained in solution by treating the hydrochloric acid solution of the tetrahydroxide with sulphur dioxide until it has become green.

Potassium Iridiochloride, $K_6Ir_2Cl_{12} + 6H_2O$, is best obtained

[1] *Ber. Deutsch. Chem. Ges.* xi. 1761.

from the corresponding iridic salt by heating it with sulphuretted hydrogen water, and allowing the olive-green solution obtained by the addition of potassium chloride to crystallize. It forms green oblique prisms which readily effloresce.

Sodium Iridiochloride, $Na_6Ir_2Cl_{12} + 24H_2O$, is obtained in a similar way to the foregoing compound and forms large olive-green or brown triclinic crystals.

Ammonium Iridiochloride, $(NH_4)_6Ir_2Cl_{12} + 3H_2O$, is obtained by evaporating the sodium salt with concentrated sal-ammoniac solution. It forms dark olive-green prisms isomorphous with the corresponding rhodium salt.

Iridious Bromide, $Ir_2Br_6 + 8H_2O$. When the blue hydroxide is dissolved in hydrobromic acid, a blue liquid is obtained which loses bromine on evaporation and deposits small, light olive-green, six-sided crystals, having the above composition. They dissolve readily in water but are not soluble in alcohol, and lose their water of crystallization at 100°. From the mother-liquor of this salt steel-gray needles of *hydrogen iridiobromide*, $H_6Ir_2Br_{12} + 6H_2O$, having a metallic lustre by reflected light are deposited. These, when heated to 100°, lose water and are converted into a brownish-red mass which is easily soluble in water and alcohol. The solution decomposes carbonates with formation of iridiobromides.

Potassium Iridiobromide, $K_6Ir_2Br_{12} + 6H_2O$, forms long olive-green lustrous four-sided needles which effloresce on exposure, becoming light-green and opaque. They readily dissolve in water.

Ammonium Iridiobromide, $(NH_4)_6Ir_2Br_{12} + 3H_2O$, is obtained by reducing the corresponding iridibromide with sulphur dioxide and neutralizing with ammonium carbonate. It crystallizes in dark olive-green prisms, and is isomorphous with the corresponding rhodium salt, with which it crystallizes in all proportions.

Iridious Sulphite, $Ir_2(SO_3)_3 + 6H_2O$, is obtained when the hydroxide, suspended in water, is treated for some time with sulphur dioxide. This compound is found in solution whilst a brown basic salt remains undissolved. The solution is then evaporated, when the normal sulphite separates out in the form of a yellow crystalline precipitate which is scarcely soluble in water but readily dissolves in dilute acids.

IRIDIC SALTS.

651 *Iridium Tetrachloride*, or *Iridic Chloride*, $IrCl_4$, is obtained by dissolving the finely-divided metal in aqua-regia, or by the solution of the blue hydroxide in hydrochloric acid. When the solution is evaporated at a temperature not above 40°, a black mass is obtained which appears red in thin films, and which contains a small quantity of sesquichloride. The hydrochloric acid solution probably contains *chloriridic acid*, H_2IrCl_6, corresponding to the following compounds.

Potassium Iridichloride, K_2IrCl_6, is obtained by the addition of potassium chloride to the hydrochloric acid solution. On evaporation small blackish-red regular octohedrons are deposited. These are slightly soluble in cold, but more readily in hot water, but do not dissolve in a saturated solution of an alkaline chloride or in alcohol.

Sodium Iridichloride, Na_2IrCl_6, is easily soluble in water, and crystallizes in almost black tables or prisms, which are isomorphous with the corresponding platinum salt.

Ammonium Iridichloride, $(NH_4)_2IrCl_6$, is obtained by precipitating the acid solution of the chloride by sal-ammoniac. It is a dark cherry-red powder, consisting of small blackish-red octohedrons.

Iridium Tetrabromide, or *Iridic Bromide*, $IrBr_4$. The blue hydroxide dissolves in hydrobromic acid, giving rise probably to *bromiridic acid*, H_2IrBr_6. This on evaporation with nitric acid leaves a blue deliquescent crystalline mass. It forms, with the other bromides, well crystallized iridibromides, such as K_2IrBr_6, which crystallizes in opaque, lustrous, blackish-blue regular octohedrons.

Iridium Tetraiodide, or *Iridic Iodide*, IrI_4, is obtained by boiling the hydrochloric acid solution of the chloride with potassium iodide. It forms a black powder, which yields, with the iodides of the alkali metals, well crystallized double compounds possessing a ruby-red colour.

IRIDIONITRITES.

652 *Iridionitrites.* These compounds have been investigated by Gibbs.[1]

Hydrogen Iridionitrite, $H_6Ir_2(NO_2)_{12} + 2H_2O$, forms light yellow, easily soluble needles.

Potassium Iridionitrite, $K_6Ir_2(NO_2)_{12} + 2H_2O$, is obtained in greenish-yellow crystals, and like the sodium compound of corresponding composition, is easily soluble in water.

When a solution of potassium iridichloride is boiled with an excess of potassium nitrite a yellow crystalline powder having the composition $3K_6Ir_2(NO_2)_{12} + K_6Ir_2Cl_{12}$ is obtained. This is but slightly soluble even in boiling water, and is not attacked by cold hydrochloric acid.

AMMONIACAL IRIDIUM COMPOUNDS.

653 These closely resemble the corresponding platinum compounds.

Iridiosammonium Chloride, $Ir(NH_3)_2Cl_2$, is obtained by heating a solution of iridious chloride with an excess of carbonate of ammonia and neutralizing the solution with dilute hydrochloric acid. It is a yellow granular body, insoluble in water. The corresponding hydroxide is not known, and of the other salts only the sulphate, $Ir(NH_3)_2SO_4$, has been prepared. This is obtained by heating the chloride with sulphuric acid, when an easily soluble orange-coloured crystalline powder is formed.

Iridiodiammonium Chloride, $Ir(NH_4)_4Cl_2$, is obtained by prolonged boiling of the preceding chloride with excess of ammonia. On cooling a whitish precipitate separates, and this is decomposed by boiling water with evolution of ammonia. The hydroxide has not been prepared. The sulphate can be obtained from the chloride, and crystallizes in rhombic prisms, which are easily soluble in hot water and deflagrate on heating.

Iridiopentammonium Chloride, $Ir_2(NH_3)_{10}Cl_6$. In order to prepare this salt a mixture of a dilute solution of ammonium iridiochloride with an equal volume of ammonia is made, and the mixture allowed to stand in a completely-filled and

[1] *Ber. Deutsch. Chem. Ges.* iv. 280.

well-closed stoppered bottle for four weeks in a warm place. The rose-red solution is then heated in a basin over the water-bath, saturated with hydrochloric acid, and evaporated. The crystalline powder which separates out is washed with cold water, and recrystallized from boiling water slightly acidified with hydrochloric acid. It is a light flesh-coloured, crystalline, very heavy, soluble powder, which, when heated with silver oxide and water, yields a rose-red alkaline solution of the hydroxide, from which the other salts may be prepared. They are flesh-coloured, crystalline, and neutral, with the exception of the carbonate, $Ir_2(NH_3)_{10}(CO_3)_3 + 3H_2O$, which has an alkaline reaction.

Iridiammonium Chloride, $Ir(NH_3)_4Cl_4$. When concentrated nitric acid is gradually added to iridiosammonium chloride it is converted into iridiammonium chloronitrate, $Ir(NH_3)_4Cl_2(NO_3)_2$. This dissolves in hot water and crystallizes in lustrous laminæ. If an excess of hydrochloric acid be added to a solution of this compound, the chloride is precipitated, crystallizing from boiling water in violet octohedrons. Silver nitrate precipitates only the half of the chlorine which it contains. If the chloronitrate be evaporated with dilute sulphuric acid, the chlorosulphate, $Ir(NH_3)_4Cl_2SO_4$, is obtained in fine greenish needles.

IRIDICYANIDES.

654 These compounds resemble the ferricyanides, and have been investigated by Martius.[1]

Iridicyanic Acid, $H_6Ir_2(C_3N_3)_4$, is obtained by decomposing the barium salt with dilute sulphuric acid. It is very soluble in water and alcohol, less so in ether, and is deposited from solution in crystalline crusts. It possesses an acid reaction and has an unpleasant taste, and from its solutions hydrochloric acid precipitates green iridic cyanide.

Potassium Iridicyanide, $K_6Ir_2(C_3N_3)_4$, is obtained by heating the metal with yellow prussiate of potash, or by fusing ammonium iridichloride with potassium cyanide, and also by the decomposition of the barium salt with potassium sulphate. It crystallizes in colourless quadratic prisms which are easily soluble in water, but insoluble in alcohol. It is a very stable

[1] *Ann. Chem. Pharm.* cxvii. 357.

body, which is not attacked when heated in chlorine or in hydrochloric acid gas.

Barium Iridicyanide, $Ba_3Ir_2(C_3N_3)_4 + 18H_2O$. In order to prepare this compound the crude potassium salt is precipitated with copper sulphate, and the precipitate decomposed with baryta water. It forms hard, transparent, probably quadratic crystals, which effloresce on exposure, are easily soluble in water, and are attacked with difficulty by acids.

IRIDIUM AND SULPHUR.

655 *Iridium Monosulphide*, IrS. The metal burns when ignited in sulphur vapour, giving rise to this compound, which resembles galena in its appearance.

Iridium Sesquisulphide, Ir_2S_3, is precipitated when sulphuretted hydrogen is passed into a solution of an iridious salt. It is a brown powder, somewhat soluble in pure water, and slightly so in potassium sulphide and nitric acid.

Iridium Disulphide, IrS_2, is formed when the powdered metal is heated with sulphur and carbonate of soda, and remains behind as a black powder when the fused mass is lixiviated.

Detection and Estimation of Iridium.

656 Sal-ammoniac produces, in a tolerably concentrated solution of iridium, a dark-red crystalline precipitate, and the dark colour sometimes observed in the corresponding platinum precipitate indicates the presence of iridium in this metal. Iridium is also distinguished from platinum by the formation of a colourless solution of potassium iridichloride when caustic potash is added to the chloride of the metal, and on exposure to the air this colourless solution first becomes red-coloured, and afterwards blue.

Sulphuretted hydrogen decolorizes the solution of an iridic salt with separation of sulphur, whilst the brown sulphide, soluble in ammonium sulphide, is precipitated.

Iridium, like platinum, is always determined quantitatively as the metal.

The *atomic weight* of iridium was determined by Berzelius[1] by a single analysis of potassium iridichloride, from which he

[1] *Pogg Ann* xiii. 435.

obtained the number 196·7. Seubert[1] has lately found, in a series of careful experiments, that the exact atomic weight is 192·7. The reason that Berzelius obtained too high a number is partly due to the fact, mentioned by himself, that his metal contained a small quantity of osmium.

RUTHENIUM, Ru = 103·5.

657 In 1828 Osann[2] stated that he had discovered three new metals in the platinum ores from the Ural. To one of these he gave the name of *ruthenium*, from the name of Russia, the country in which it was found. In the following year, however, he withdrew the statement of the existence of one of the metals, and the existence of the other two remained doubtful until Claus, in 1845, examined the question. This chemist proved the existence of a new metal in the platinum ore, and retained for it the name of ruthenium because it was found to be contained in small quantity in the substance termed ruthenium oxide by Osann, which for the most part consisted of silica, zirconia, and the oxides of titanium and iron. We owe almost the whole of our knowledge respecting this metal to Claus.[3]

Ruthenium is found both in platinum ore and in osmiridium, whilst it occurs as sulphide in laurite, Ru_2S_3.[4]

Of the various methods of preparing the metal, that of Deville and Debray[5] is the most interesting, as these chemists prepared the metal on a large scale, and specially studied its physical properties. For this purpose, the alloy of osmiridium containing ruthenium is fused with zinc, the regulus then treated with hydrochloric acid, and one part of the finely-divided residue mixed with three parts of barium dioxide and one part of barium nitrate, the mixture being heated for two hours to a temperature somewhat below the melting-point of silver. The cold mass is then reduced to an impalpable powder and thrown into dilute hydrochloric acid contained in a stoppered bottle. In this operation the liquid must be kept well cooled in order to prevent the escape of the vapours of poisonous osmium tetroxide, and the operation must be carried on in a good draught-place. As soon as the

[1] *Chem. Soc. Journ.* 1879, i. 125.
[2] *Pogg. Ann.* xiv. 329 ; lxiv. 197.
[3] *Ann. Chem. Pharm.* lvi. 257 ; lix. 234 ; *Pogg. Ann.* lxiv. 622 ; lxv. 200 ; *Jahresb.* 1859, 257 ; 1860, 205 ; 1861, 320 ; 1863, 397.
[4] Wöhler, *Ann. Chem. Pharm.* cxxix. 116.
[5] Deville and Debray, *Compt. Rendus*, lxxxiii. 926.

action is over, one part of nitric acid and two parts of sulphuric acid are added to the liquid, the mixture well shaken, the barium sulphate allowed to deposit, and the clear liquid poured off. The residue is washed by decantation and the liquid distilled until three-fourths of it have passed over. The distillate is worked up for osmium, whilst the concentrated residue, mixed with from two to three parts of sal-ammoniac and a small quantity of nitric acid, is dried on the water-bath. The residue is then washed with water which is half saturated with sal-ammoniac, until the filtrate is colourless. By this treatment ammonium iridichloride, containing some ruthenium, remains behind. This is ignited and the remaining spongy metallic mass fused for two hours in a silver basin with two parts of nitre and one part of caustic potash. The fused mass is then dissolved in water, and the characteristic orange-red solution of ruthenate of potassium treated with nitric acid until the yellow colour has disappeared, when ruthenium oxide separates out, which, however, still contains silicic acid and some iridium and osmium; it is then ignited in a graphite crucible and fused in the oxyhydrogen furnace.

Another plan for preparing chemically pure ruthenium depends upon the facts that whilst osmium tetroxide is volatilized in a stream of air, the corresponding and volatile tetroxide of ruthenium is only formed by the action of chlorine in alkaline solution of ruthenium. Hence the metal, as obtained by other processes, must be heated in a current of oxygen until the whole of the osmium tetroxide has been volatilized and then fused a second time with potash and saltpetre, the mass dissolved in water, saturated with chlorine, and distilled in a stream of chlorine on the water-bath, when pure ruthenium tetroxide volatilizes. This is then dissolved in caustic potash and the ruthenium sesquioxide precipitated from this solution by alcohol, and this again reduced to metal by ignition in a stream of coal-gas or hydrogen.

In order to obtain the metal in the crystalline state it may be fused in a carbon crucible with from five to six times its weight of tin, the alloy being treated with boiling hydrochloric acid which leaves the compound $RuSn$ undissolved; this when ignited in a carbon-boat in a current of hydrochloric acid gas leaves a residue of crystallized ruthenium. Of all the platinum metals, osmium alone excepted, ruthenium combines with oxygen most readily.

Ruthenium has a specific gravity of 12·261 at 0°; like iridium it is hard and brittle, and next to osmium is the most difficultly fusible metal of this group. The fused metal oxidizes slowly in the air, becoming covered with a brown film, and on cooling from a state of fusion it spirts like iridium. The pure metal is scarcely attacked even by aqua-regia, but it combines with chlorine at a red heat.

RUTHENIUM AND OXYGEN.

658 Ruthenium forms no less than six oxides, namely, RuO, Ru_2O_3, RuO_2, RuO_3, Ru_2O_7, RuO_4; the oxides RuO_3 and Ru_2O_7 are, however, only known in a state of combination.

Ruthenium Monoxide, RuO. If the finely-divided metal be frequently powdered, and after each pulverization ignited in chlorine, the dichloride of ruthenium is obtained as a black, partially crystalline mass, insoluble in acids. By calcining the dichloride mixed with carbonate of soda in a current of carbon dioxide and washing the residue with water, ruthenium monoxide remains as a dark-grey powder, which is not attacked by acids.

Ruthenium Sesquioxide, Ru_2O_3, is formed when the finely-divided metal is heated to redness for some time in contact with the air. It is a deep-blue coloured powder, insoluble in acids. It does not lose oxygen even at a white-heat, but is readily reduced by ignition in hydrogen.

Ruthenium Sesquihydroxide, $Ru_2(OH)_6$, is obtained by precipitating the corresponding chloride with an alkali. It forms a blackish-brown precipitate, which even after long washing retains from three to four per cent. of alkali. It dissolves with a yellow colour in acids, but is insoluble in water and alkalis.

Ruthenium Dioxide, RuO_2. This is obtained by roasting the disulphide or sulphate in contact with air. It is likewise formed when the metal is fused in an oxidizing atmosphere, when it burns with a sparkling smoky flame, and evolves an ozone-like smell. Hence this compound can be easily obtained from the ruthenium contained in the osmiridium alloy, which may for this purpose be heated in a porcelain tube to the melting-point of copper, in a current of pure air, from which all organic substance has previously been carefully separated. The ruthenium dioxide is carried forward by the osmium tetroxide formed at the same time, and

deposited in the cold part of the tube, whilst the more volatile osmium compound is carried on still further by the current of air. Ruthenium dioxide crystallizes in small very hard quadratic pyramids, possessing a green metallic lustre, and a bluish or greenish iridescence. These have a specific gravity of 7·2, and are isomorphous with cassiterite and rutile (Rammelsberg).

Ruthenium Tetrahydroxide, $Ru(OH)_4 + 3H_2O$, is obtained by evaporating ruthenium disulphate with caustic potash, when a dark-red precipitate falls down. This contains some alkali, and dries to a reddish-brown mass, giving off water at 300°. When more strongly heated it deflagrates with vivid incandescence and evolution of a black soot-like smoke. It is soluble in acids and alkalis, yielding yellow solutions.

Ruthenium Trioxide does not exist in the free state. Some of its salts are, however, known. Thus, the potassium salt is obtained by igniting ruthenium with a mixture of potash and nitre or chlorate of potash. This salt, termed potassium ruthenate, dissolves in water with a reddish-yellow colour, has a taste as astringent as that of tannic acid, and colours organic substances black.

Ruthenium Peroxide, Ru_2O_7, is not known in the free state, nor has the corresponding *per-ruthenic acid*, H_2RuO_4, been obtained. The potassium salt has been prepared by Deville and Debray[1] by acting with chlorine on potassium ruthenate. From the dark-green solution which is thus formed, small black lustrous rhombic pyramids separate out isomorphous with potassium permanganate. The blackish-green solution soon becomes yellow, giving rise to potassium ruthenate and the following oxide.

Ruthenium Tetroxide, RuO_4. This oxide is very volatile, corresponding in this respect to osmium tetroxide. It is obtained by passing chlorine into a solution of potassium ruthenochloride or potassium ruthenate, this latter being prepared by fusing a mixture of three grams of ruthenium with twenty-four grams of caustic potash and eight grams of nitre to redness in a silver crucible. The mass is dissolved in forty-eight grams of water, and this solution brought into a tubulated retort, having a long condensing tube attached to it, and dipping into a flask containing caustic potash. Chlorine is then passed into the liquid, which becomes heated, and the volatile ruthenium tetroxide passes over. This

[1] *Compt. Rend.* lxxxiii. 926.

deposits in the neck of the retort and in the condensing tube in the form of a golden-yellow crystalline crust consisting of glistening rhombic prisms. They possess an astringent but not an acid taste. The tetroxide melts at 40°, yielding a liquid which boils slightly above 100°, and gives rise to a golden-yellow vapour, which emits an odour resembling that of nitrous fumes, and produces coughing and great irritation of the mucous membrane (Claus). In the year 1875 Deville and Debray[1] endeavoured to distil 150 grams of this liquid; an evolution of gas began at 108°, and a few moments afterwards a frightful explosion occurred, the whole laboratory being filled with a strong smell of ozone, and a black soot-like smoke, as if turpentine had been burned.

The moist oxide decomposes in a few hours into oxygen and the sesquioxide, but in the dry state it may be preserved undecomposed for a longer time. It dissolves slowly and with difficulty in water. The solution, when it contains free chlorine, may be preserved for some days in the dark without undergoing alteration, but on exposure to light decomposition rapidly takes place. It blackens the skin as well as other organic bodies, and alcoholic potash immediately reduces it, finely-divided metallic ruthenium being thrown down.

RUTHENIOUS SALTS.

659 The ruthenious salts are derived from the sesquioxide, and of these only a few of the haloid compounds are known. The chloride and its double salts dissolve in water with a reddish-yellow colour. This solution deposits on standing, slowly in the cold but quickly when warmed, a black very finely-divided precipitate of oxychloride. This reaction is so delicate that one part of the metal imparts a distinct ink-like colour to 100,000 parts of water.

Ruthenious Chloride or *Ruthenium Sesquichloride*, Ru_2Cl_6, is obtained by evaporating a solution of the hydroxide in hydrochloric acid. Thus prepared it is a deliquescent mass, possessing an astringent but not a metallic taste.

Potassium Rutheniochloride, $Ru_2K_4Cl_{10}$, is prepared by mixing solutions of the two chlorides. It is difficultly soluble in cold, though readily in hot water. It forms a violet-brown

[1] *Ann. Chim. Phys.* [5], iv 537.

iridescent crystalline powder, consisting of microscopic orange-red glistening cubes. The solution possesses a purely astringent taste.

The ammonium salt prepared in a similar way possesses analogous properties.

Ruthenious Iodide, Ru_2I_6, is a black precipitate formed on the addition of potassium iodide to a solution of potassium ruthenochloride. It separates slowly in the cold, but quickly on heating.

RUTHENIC SALTS.

660 *Ruthenic Chloride* or *Ruthenium Tetrachloride*, $RuCl_4$. On evaporating a solution of the corresponding hydroxide in hydrochloric acid, a reddish liquid is obtained, and a reddish-brown hygroscopic mass is at last left behind. This dissolves in water and in alcohol, yielding a cinnabar-coloured solution, and possessing a bitter taste.

Potassium Ruthenichloride, K_2RuCl_6, is obtained when mixed solutions of ruthenic chloride and potassium chloride are evaporated. On crystallization from hot water the compound is obtained in red regular octohedrons, and is more readily soluble in water than any of the other corresponding potassium salts of this group. It is only slightly soluble in concentrated solutions of sal-ammoniac, and is insoluble in alcohol.

The corresponding ammonium salt crystallizes, when its solution is quickly cooled, in small dark-red prisms, but when slowly deposited it forms dark cherry-red octohedrons.

Ruthenic Sulphate, $Ru(SO_4)_2$, is obtained by dissolving the sulphide in nitric acid. The reddish-yellow solution leaves on evaporation a yellowish-brown amorphous mass which yields a deliquescent powder closely resembling mosaic gold.

AMMONIACAL COMPOUNDS OF RUTHENIUM.

661 *Rutheniosammonium Hydroxide*, $Ru(NH_3)_2(OH)_2$, is obtained by evaporating a solution of the rutheniodiammonium hydroxide, $Ru(NH_3)_4(OH)_2$, in a vacuum over sulphuric acid. It is a yellowish-brown, spongy mass, consisting of small very deliquescent laminæ, containing five molecules of water. It

possesses a strongly alkaline reaction, and acts as a strong caustic, giving rise to painful wounds when brought on to the tongue. Its salts are of a dark-yellow colour, and have been but slightly examined.

Rutheniodiammonium Chloride, $Ru(NH_3)_4Cl_2$, is obtained by boiling ammonium ruthenichloride with an excess of ammonia until the dark-red solution becomes of a golden-yellow colour. It crystallizes in golden-yellow oblique rhombic crystals, which taste like potassium chloride, and are not very soluble in cold water and insoluble in alcohol. When the solution is warmed, and silver oxide added, a yellow, strongly alkaline liquid, having a very caustic taste, is formed. This acts upon the tongue in a similar way to the preceding compound, and exhibits the same reactions as caustic potash with the various metallic salts. Platinic chloride precipitates the solution of this chloride, the compound $Ru(NH_3)_4PtCl_6$ being thrown down in yellow microscopic needles.

Rutheniodiammonium Sulphate, $Ru(NH_3)_4SO_4 + 4H_2O$, is obtained by decomposing the chloride with silver sulphate. It crystallizes in fine transparent rhombic plates, having a golden-yellow colour, which give off water on exposure to the air, and assume a metallic lustre.

Rutheniodiammonium Carbonate, $Ru(NH_3)_4CO_3 + 5H_2O$, is formed by heating the chloride with silver carbonate. It crystallizes in light-yellow rhombic prisms, having a strongly alkaline reaction, and is easily soluble in water, though insoluble in alcohol.

RUTHENIOCYANIDES.

662 These compounds correspond to the ferrocyanides. The potassium salt is obtained by fusing ammonium ruthenichloride with potassium cyanide.

Rutheniocyanic Acid, $H_8Ru(C_3N_3)_4$, is obtained by acting with hydrochloric acid and ether on the solution of the potassium salt. It crystallizes in colourless pearly laminæ, easily soluble in water and alcohol. The solution possesses an acid reaction and an astringent taste, and on exposure to air assumes a blue colour (Claus).

Potassium Rutheniocyanide, $K_8Ru_2(C_3N_3)_4+6H_2O$, forms colourless crystals, isomorphous with yellow prussiate of potash. Its

solution is turned a bright-violet colour by ferrous sulphate, and a dark-violet by ferric salts, whilst the salts of mercury, lead, and zinc yield white precipitates.

RUTHENIUM AND SULPHUR.

Ruthenium Sesquisulphide, Ru_2S_3, occurs as laurite, found with platinum-ore in Borneo and Oregon. It crystallizes in small octohedrons, having the faces of the cube, and showing an octohedral cleavage. It usually contains a small percentage of osmium. Solutions of the ruthenium salts yield a brown precipitate with sulphuretted hydrogen, and this when dried in a current of carbon dioxide yields the sesquisulphide as a dark metallic powder.

Detection and Estimation of Ruthenium.

663 The ruthenic salts are precipitated dark-red by concentrated solutions of potassium chloride and ammonium chloride, and on boiling with water the characteristic ruthenium oxychloride is formed. Ruthenium solutions are first coloured blue by sulphuretted hydrogen, and afterwards the brown sulphide is formed, which is almost insoluble in ammonium sulphide. The production of the volatile tetroxide is also a characteristic reaction.

Ruthenium, like the other members of this group, is estimated quantitatively as the metal.

The *atomic weight* of ruthenium has been determined by Claus,[1] to whom we are also indebted for the investigation of almost all the ruthenium compounds. He found it to be 103·5.

OSMIUM, Os = 198·6.

664 The mode of occurrence of this metal has already been described. It may be easily separated from the other members of the platinum group by means of its property of combining directly with oxygen to form a very volatile tetroxide, OsO_4. This compound is obtained, in a more or less pure state, in the

[1] *N. Petersb. Acad. Bull.* i. 102.

course of the preparation of the other platinum metals, and especially of ruthenium (see page 449). The solution thus obtained may be precipitated with ammonia and ammonium sulphide, and the precipitate mixed with sodium chloride, and heated in a slow current of chlorine. The mass when lixiviated yields sodium osmichloride, $(NH_4)_2OsCl_6$, and from this solution ammonium-osmichloride is thrown down by sal-ammoniac. This is next washed with sal-ammoniac solution, and then heated in a covered crucible, when spongy osmium is obtained.

Pure osmium was obtained by Deville and Debray,[1] by passing the vapour of the pure tetroxide mixed with carbon monoxide and carbon dioxide through a red-hot porcelain tube. Thus prepared, the metal assumes the form of an amorphous powder, which is converted into the crystalline variety when fused with from three to four times its weight of tin in a charcoal crucible, the crystalline alloy treated with hydrochloric acid, and the residue heated in a current of hydrochloric acid gas.

The crystalline form of osmium is either that of the cube or of a very obtuse rhombohedron. The crystals possess a bluish-white colour with violet lustre, are harder than glass, and possess a specific gravity of 22·477. Hence osmium is the heaviest of known bodies. Osmium has not yet been fused. When it is heated up to the temperature at which iridium is fully melted it evaporates, and deposits in the form of a black powder on a cold surface held in the vapour, whilst it takes fire in the air, and forms the tetroxide.

The experiment of volatilizing osmium in the oxyhydrogen furnace is one accompanied by great danger. Deville, who performed the operation twice, was rendered almost blind for twenty-four hours by having accidentally become exposed to the vapour of the tetroxide. This substance produces the most violent pain and inflammation of the conjunctiva, and vision is permanently injured by the subsequent reduction of a film of metallic osmium.[2] Osmium is not used in the arts, but the alloy of osmiridium, which is not attacked by acids, is employed for tipping gold pens, and, inasmuch as it is unoxidizable and non-magnetic, it has been employed for the bearings of the mariner's compass.

1 *Compt. Rend.* lxxxii. 1076. 2 *Ann. Chim. Phys.* [3], lvi. 400.

OXIDES AND SALTS OF OSMIUM.

665 The following oxides are known:

Osmium Monoxide, OsO.
Osmium Sesquioxide, Os_2O_3.
Osmium Dioxide, OsO_2.
Osmium Tetroxide, OsO_4.

In addition to these the salts of osmic acid, H_2OsO_4, are known, but neither the acid nor the corresponding oxide, OsO_3, have been prepared.

The several oxides and their corresponding compounds will be dealt with together.

Osmium Monoxide, OsO, is obtained when the corresponding sulphite mixed with carbonate of soda is ignited in a current of carbon dioxide. It is a greyish-black powder insoluble in acids.

Osmium Sulphite, $OsSO_3$. In order to prepare this salt, sulphur dioxide is led into an aqueous solution of the peroxide, and glauber-salt added to the blue liquid. The dark-blue precipitate, after washing, is dried and yields a powder which is unalterable in the air, and which on trituration exhibits a metallic silvery lustre. If the blue solution be treated with caustic potash a blackish-blue precipitate of hydroxide is obtained, which on exposure to air absorbs oxygen as rapidly as ferrous hydroxide.

Potassium Osmium Sulphite, $H_2K_6Os(SO_3)_5 + 4H_2O$, is obtained by heating the solution of potassium osmiochloride with potassium sulphite. It is a crystalline pale rose-red precipitate.

Osmium Sesquioxide, Os_2O_3, is a black powder insoluble in acids obtained by heating its salts with carbonate of soda in a current of carbon dioxide. Of these the two following have been most accurately examined.

Deville and Debray obtained this oxide in copper-red scales, together with the metal, by the reduction of the tetroxide.

Potassium Osmiochloride, $K_6Os_2Cl_{12} + 6H_2O$, is obtained by adding ammonia to a solution of osmium tetroxide in caustic potash, and saturating the liquid, as soon as it has become yellow, with hydrochloric acid. On evaporation, the above salt separates out together with potassium chloride

and sal-ammoniac. This latter can be readily separated mechanically. It forms dark-red crystals which effloresce in the air and become pink. It dissolves in water, yielding a cherry-red coloured solution, possessing first a strongly astringent, and then a sickly sweetish taste.

Ammonium Osmiochloride, $(NH_4)_6Os_2Cl_{12} + 3H_2O$. In order to prepare this salt sulphuretted hydrogen is passed into a hydrochloric acid solution of the tetroxide until it has become red. The liquid is then evaporated with sal-ammoniac, when fine red crystals are deposited resembling the potassium salt.

Alkalis precipitate a brownish-red hydroxide from solutions of these salts.

Osmium Dioxide, OsO_2, is obtained from its salts in a similar way to the foregoing oxides. It is likewise formed when its hydroxide is heated in a current of carbon dioxide. Prepared in this way it forms masses having a coppery lustre. It does not decompose in absence of air even at a red-heat, but when mixed with combustible bodies it deflagrates on heating.

Osmium Tetrahydroxide, $Os(OH)_4$, is produced when the aqueous solution of the tetroxide is mixed with alcohol or other reducing agent, or when potassium osmate is treated with nitric acid:

$$2K_2OsO_4 + 4HNO_3 = Os(OH)_4 + OsO_4 + 4KNO_3.$$

It is a black precipitate which dries up to a heavy brown mass having a coppery lustre. When freshly precipitated it is tolerably soluble in hydrochloric acid. When heated in nitrogen to 200° it is converted into $OsO(OH)_2$. Only a few of its salts have been accurately examined, as they rapidly undergo decomposition in solution.

Osmium Tetrachloride, $OsCl_4$, is obtained by heating the metal in dry chlorine. It forms a red sublimate which dissolves in water, yielding a yellow solution; and this on dilution with more water attains a green tint. On standing the solution becomes colourless with separation of lower oxides, whilst hydrochloric acid and osmium tetroxide remain in solution.

Potassium Osmichloride, K_2OsCl_6, is obtained by gently heating a mixture of the finely-divided metal with potassium chloride in a current of chlorine, and also by evaporating the hydrochloric acid solution of the tetroxide with potassium chloride. It crystallizes in dark-brown glistening octohedrons, which yield a cinnabar-red powder, and dissolve in water with a

yellow colour. Alcohol precipitates the compound from this solution in the form of a red crystalline powder.

Sodium Osmichloride, $Na_2OsCl_6 + 2H_2O$, is obtained in a similar way, and crystallizes in long orange-coloured prisms which are easily soluble in water and alcohol.

Ammonium Osmichloride, $(NH_4)_2OsCl_6$, is obtained by the addition of powdered sal-ammoniac to a solution of the sodium salt. It then deposits as a red crystalline powder, crystallizing from dilute solution in brown octohedrons.

Osmium Trioxide, OsO_3, and *Osmic Acid*, H_2OsO_4, are neither of them known in the free state. In this respect osmium resembles manganese.

Potassium Osmate, $K_2OsO_4 + 2H_2O$, is obtained on the addition of alcohol or other reducing agent to the solution of the tetroxide in caustic potash. The liquid then becomes of a fine red colour, and when it is sufficiently concentrated the salt separates out as a crystalline powder. When slowly crystallized it forms octohedrons which according to their size are of a garnet-red or almost black colour. They possess a sweet astringent taste, and do not undergo change on exposure to dry air, but both in solution and in moist air they decompose, especially on addition of an acid, with formation of tetroxide and lower oxides.

The *sodium* salt crystallizes less easily, and yields an aqueous solution having a rose-red colour, from which barium chloride precipitates $BaOsO_4$ as an amorphous green flocculent precipitate, which after a while changes to black shining prismatic crystals.

Osmium Tetroxide (commonly called osmic acid), OsO_4. Very finely-divided metallic osmium oxidizes slowly at the ordinary temperature, and at about 400° takes fire with formation of the above oxide. The denser the metal the higher is the temperature needed for oxidation. Osmium tetroxide is also produced when the metal is heated in a current of steam, and also by dissolving the lower oxides or the metal in nitric acid or aqua-regia. These reagents however do not attack the metal after it has been strongly ignited. Osmium tetroxide sublimes in transparent glistening needles which become soft and may be moulded in the hand like wax, and melt at a lower temperature than this substance. They begin to sublime at a very moderate heat, and the fused oxide boils at 100°, yielding a colourless vapour having a specific gravity of 8·89. The crystals readily dissolve in water, forming a colourless liquid which does not redden litmus paper, and possesses a caustic and burning taste. It has

a most powerful penetrating smell, somewhat analogous to that of chlorine and iodine. A very small quantity of vapour mixed with air attacks the lungs, giving rise to very serious inflammation of the mucous membranes. As an antidote to the effects of the osmic acid Claus recommends the inhalation of sulphuretted hydrogen, which however must be cautiously employed. Osmium tetroxide also acts violently on the skin, causing a painful eruption which can be removed by the use of sulphur baths. The vapour also acts, as has been stated, most violently on the eyes, and may produce most serious consequences.[1]

When heated on red-hot charcoal it deflagrates like nitre. It is easily converted into lower oxides by reducing substances, and its alkaline solution when boiled with a salt of formic acid is precipitated of a blue colour. If osmium tetroxide be dissolved in alcohol or ether, the whole of the osmium precipitates on standing for twenty-four hours as the tetrahydroxide. Sulphur dioxide colours the aqueous solution yellow, then brown, green, and at last indigo-blue.

OSMIAMIC ACID AND ITS SALTS.

666 *Osmiamic Acid*, $H_2N_2Os_2O_5$, is formed by the action of ammonia on the tetroxide, especially in the presence of potash, because the potassium salt is more stable than the ammonium compound :

$$2OsO_4 + 2NH_3 + 2KOH = K_2N_2Os_2O_5 + O + 4H_2O.$$

The free acid is obtained by decomposing the barium salt with dilute sulphuric acid, or the silver salt with hydrochloric acid. The light-yellow solution remains in the dilute state without change for some time. In the concentrated condition, however, it decomposes with evolution of gas and separation of a brown powder.[2]

Potassium Osmiamate, $K_2N_2Os_2O_5$, forms orange-yellow quadratic pyramids, which dissolve slowly in cold, and more readily in hot water, and on recrystallization become dark-coloured, owing to partial decomposition.

The *sodium* salt is more readily soluble, and crystallizes in

[1] Deville and Debray, *Ann. Chim. Phys.* [3], lvi. 400 ; *Comptes Rendus*, lxxviii. 1509.

[2] Fritzsche and Struve, *Petersb. Acad. Bull.* vi. 81.

large prisms. It is best obtained by the decomposition of the silver salt with sodium chloride. The *barium* salt, $BaN_2Os_2O_5$, which forms glistening yellow easily-soluble needles, is obtained by a similar reaction.

Silver Osmiamate, $Ag_2N_2Os_2O_5$, is obtained when nitric acid is added to a solution containing the tetroxide and silver nitrate dissolved in ammonia. It is a difficultly-soluble orange-yellow crystalline powder, which detonates on percussion or when heated.

AMMONIACAL OSMIUM COMPOUNDS.

667 *Osmioxyammonium Hydroxide*, $Os(NH_3)_2O(OH)_2$, is obtained by dissolving the tetroxide in an excess of concentrated ammonia, and heating the reddish-yellow solution in a closed vessel to 50°, when a black precipitate is formed. The flask is then opened and the solution evaporated at a low temperature until the excess of ammonia has been driven off. The base is thus obtained in the form of a blackish-brown powder, which when heated decomposes with rapid evolution of gas. With acids it forms amorphous salts.

Osmioxydiammonium Chloride, $Os(NH_3)_4O_2Cl_2$, is obtained on the addition of sal-ammoniac to a solution of potassium osmate, in the form of a yellow crystalline precipitate easily soluble in water, the solution soon undergoing decomposition.

OSMIOCYANIDES.

668 The osmiocyanides correspond closely in composition and in their properties to the ferrocyanides. The most important of these compounds are the following:

Osmiocyanic Acid, $H_8Os_2(C_3N_3)_4$, is deposited in the form of white scales on the addition of fuming hydrochloric acid to a solution of the potassium salt. These are easily soluble in alcohol, and crystallize out from the alcoholic solution on the addition of ether in colourless glistening transparent hexagonal prisms. Its aqueous solution has an acid reaction, and from it osmious cyanide, $Os(CN)_2$, separates out as a dark-violet precipitate.

Potassium Osmiocyanide, $K_8Os_2(C_3N_3)_4 + 6H_2O$, is obtained by dissolving potassium osmate in potassium cyanide, evaporating,

and fusing the residue. It crystallizes from hot water, in which it is easily soluble, in yellow quadratic tables, which when heated give off water and become colourless. Its solution yields a light-blue precipitate with ferrous salts, which becomes darker-coloured on exposure to air, and when treated with nitric acid it is converted into a fine violet-coloured powder, which is also obtained by precipitating the potassium salt with ferric chloride. After drying it forms a fragile mass having a copper-red colour, and when boiled with caustic potash it yields ferric hydroxide and potassium osmiocyanide.

Barium Osmiocyanide, $Ba_4Os(C_3N_3)_4 + 6H_2O$, is formed when the iron precipitate is boiled with baryta-water. It crystallizes in small yellowish-red transparent rhombic prisms, which are easily soluble in water and alcohol.

Potassium Barium Osmiocyanide, $K_4Ba_2Os_2(C_3N_3)_4 + 6H_2O$, is obtained by mixing hot solutions of the potassium and barium salts. On cooling small yellow oblique rhombohedrons are deposited, which are difficultly soluble in cold water.

OSMIUM AND SULPHUR.

Metallic osmium burns when heated in sulphur vapour, and sulphuretted hydrogen throws down a dark-yellow sulphide of osmium from the hydrochloric acid solution of the oxide. This is slightly soluble in water, giving rise to a dark-yellow solution, and easily dissolves in nitric acid.

When sulphuretted hydrogen is passed through an aqueous solution of osmium tetroxide a brown precipitate of osmium tetrasulphide, OsS_4, is thrown down. This is not soluble in alkalis, or in the sulphides of the alkali metals.

Detection and Estimation of Osmium.

669 The presence of this metal may be most easily detected by the formation of the volatile strongly-smelling tetroxide. Sulphuretted hydrogen throws down a precipitate of the sulphide, insoluble in sulphide of ammonium. If a solution contain a mixture of the platinum metals, and other metals precipitable by sulphuretted hydrogen, this gas is passed into the hot solution so long as a precipitate is formed. This is then washed and warmed with yellow sulphide of ammonium, when platinum,

iridium, gold, &c., dissolve. The filtrate is then acidified with hydrochloric acid, the precipitate fused with sodium carbonate and sodium nitrate, and the fused mass lixiviated with water, the residue being treated according to the method already described under platinum (see page 421). In this way the iridium is obtained together with platinum and gold, and these may be readily separated. The portion insoluble in sulphide of ammonium is then fused with caustic potash and potassium chlorate, and treated with water in order to dissolve the potassium salts of ruthenic and osmic acids. The solution is carefully neutralized with nitric acid in order to separate the black oxide of ruthenium, and the filtrate distilled with nitric acid, when the volatile osmium tetroxide passes over. The residue insoluble in water is gently ignited in a current of hydrogen, treated with dilute nitric acid, when palladium and rhodium remain behind, and these are separated by aqua-regia, in which the latter metal is insoluble.

Osmium is usually estimated *quantitatively* as the metal. It is separated from other metals as the volatile tetroxide, the vapours of which, in order to avoid loss, are passed into caustic potash; and alcohol is added to the distillate in order to form potassium osmate, and the solution then treated with sal-ammoniac and the precipitated osmioxydiammonium chloride ignited in hydrogen when the metal is obtained.

The *atomic weight* of osmium was determined by Berzelius in a similar way to that of platinum, and he obtained the number 198·3, whilst Claus and Jakoby,[1] who investigated many of the osmium compounds, obtained the number 198·9. The mean of the two estimations is 198·6.

[1] *N. Petersb. Acad. Bull.* vi. 152.

SPECTRUM ANALYSIS.

670 THE following pages contain a short statement of the principles of spectrum analysis, and of the application of these principles to the detection of certain elementary and compound bodies. A complete treatise on spectrum analysis would here be out of place; for the subject has not only now outgrown the space which can be assigned to it in a work like the present, but much diversity of opinion is still expressed on various important points, and a discussion of these views cannot here be attempted.

The spectroscope, next to the balance, is the most useful and important instrument which the chemist possesses. Although it has only been employed for chemical investigations since the year 1860, it has been the means of effecting some of the most striking discoveries of modern times. By the help of the spectroscope the chemist is able to investigate the composition of terrestrial matter with a degree of exactitude hitherto undreamt of, and the discovery of the following new elementary bodies are the first-fruits of the employment of this instrument in chemical analysis:

Cæsium and Rubidium, by Kirchhoff and Bunsen.
Thallium, by Crookes.
Indium, by Reich and Richter.
Gallium, by Lecoq de Boisbaudran.
Ytterbium, by Marignac.
Decipium and Philipium, by Delafontaine.
Scandium, by Nilson.

In addition to this, the application of the methods of spectrum analysis to the investigation of the nature of the light emitted by the heavenly bodies has opened out a completely new field of research, and has laid the foundations of a new science, that of *Celestial Chemistry*. Such has been the progress recently

made in this direction that we are now not only assured of the existence of many of our well-known terrestrial metals in the atmospheres of the sun and the fixed stars, but we have gained a knowledge of the physical condition of our luminary such as we formerly could not have thought possible, and have even been able to form a definite opinion concerning the physical and chemical constitution of the nebulæ.

Further research has also shown that spectrum analysis, which, to begin with, was confined to the qualitative detection of chemical bodies, may possibly be made to yield quantitative results, so that a mere glance through a spectroscope may suffice to obtain a knowledge of the exact quantitative relations existing between various substances whose spectra are under examination.[1]

Moreover, it would appear that the time is not far distant when the results of spectrum observations may lead to most interesting and important conclusions respecting the molecular condition of matter, especially at temperatures far exceeding those to which our experiments have hitherto been confined, and to spectrum analysis we must also turn for assistance in our endeavours to answer the important question, Are the elements really undecomposible bodies? Spectroscopic and other evidence in favour of this view has recently been put forward by Lockyer.[2] The subject is still under examination, but as yet the evidence adduced of the compound nature of the elements is not of a sufficiently conclusive character to warrant its introduction into these pages.

671 The principles upon which spectrum analysis is founded are simple enough. When any number of solid or liquid bodies are gradually heated they will all be seen to become luminous at the same temperature. If the light which these bodies emit, when they begin to glow or become luminous, be examined by means of a prism, and suitable optical arrangements, we observe that the rays of least refrangibility, viz. the red rays, are first seen, and that, as the temperature rises, light of greater refrangibility is gradually emitted, until at last the body gives off blue or violet rays. When this point is reached the substance appears to the naked eye to be white-hot, as all the differently coloured rays, when brought together on to the retina, produce the effect

[1] Lockyer and Roberts, *Proc. Roy Soc.* xxi. 507.

[2] "Discussion of the Working Hypothesis that the so called Elements are Compound Bodies," *Pro. Roy. Soc.* Dec. 12, 1878, xxviii. 157.

which we term white light. It is thus clear that the spectrum of every incandescent solid or liquid is the same, a bright continuous coloured band, whose rays extend without a break through all the colours of the rainbow from red to violet. The case is, however, quite different with glowing gases. The light which these bodies emit does not consist, within a certain limit, of light of all degrees of refrangibility. The spectrum of a glowing gas, instead of being continuous, is more or less broken up. Incandescent gases only emit rays of definite degrees of refrangibility, and their spectra consist, therefore, of bright lines whose position undergoes no change when the temperature is increased. Thus the vapour of sodium emits a yellow light

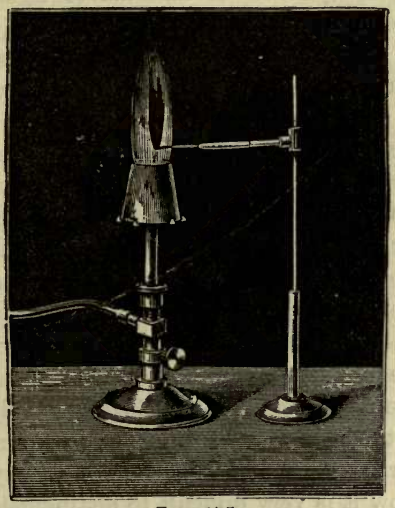


Fig. 175.

and its spectrum consists of a double yellow line having wave-lengths of 5895 and 5889 ten-millionths of a millimeter, and being coincident with the dark lines in the solar spectrum termed by Fraunhofer the D lines. These two bright sodium lines do not alter their position when the temperature of the vapour is raised; sodium vapour, as soon as it becomes luminous, glows with a yellow light, and by no increase of temperature can it be made white-hot. The peculiar colour of incandescent sodium vapour is best seen by placing, in the non-luminous gas-flame, a small bead of chloride of sodium fused on to the end of a fine platinum wire. The salt volatilizes, and the flame is coloured intensely yellow (Fig. 175).

672 Melville, in 1752, was the first to notice this yellow sodium flame, but he was unacquainted with its cause. In the year 1822, Sir David Brewster introduced his monochromatic lamp, the first idea being, however, due to Melville. In this same year Sir John Herschel investigated the spectra of many coloured flames, especially those obtained by means of the chlorides of copper and strontium, as well as by boracic acid, and in 1827 he writes concerning these observations—"the colour thus contributed by different objects to flame affords in many cases a ready and neat way of detecting extremely minute quantities of them." Again, Fox Talbot writes as follows in 1826:—"The red fire of the theatres gave a most beautiful spectrum, with many lines or maxima of light. In the red these lines were more numerous, and crowded with dark spaces between them, besides an exterior ray greatly separated from the rest, and probably due to the nitre in the composition. In the orange was one bright line, one in the yellow, three in the green, and several that were fainter." The extreme delicacy of the sodium reaction and the universal distribution of this element were facts unknown to Talbot, and he consequently attributes the yellow line first to sulphur and afterwards to the presence of water. He adds, "if this opinion"—as to the cause of the production of the lines—"should prove correct and applicable to the other definite rays, a glance at the prismatic spectrum of a flame might show it to contain substances which it would otherwise require a laborious chemical analysis to detect." In 1834 Talbot again writes:—"Lithia and strontia are two bodies characterized by the fine red tint which they communicate to the flame. Now it is very difficult to distinguish the lithia-red from the strontia-red by the naked eye, but the prism betrays between them the most marked distinction which can be imagined. The strontia flame exhibits a great number of red rays well separated from each other by dark intervals, not to mention an orange and a very definite bright blue ray. The lithia exhibits one single red ray. Hence I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty as, if not more than any known method."

In the year 1845 Dr. Wm. Allen Miller published the results of experiments on the spectra of coloured flames, together with drawings, but owing to the fact that in these researches a luminous flame was made use of, the representations of the

several spectra are wanting in clearness and individuality. Swan was the first to point out that the bright yellow line coincident with Fraunhofer's D, which was seen in every flame, is caused by the presence of sodium salts, and it is to him that we are indebted for the discovery of the extreme delicacy of the sodium reaction, and for the proof of the universal distribution of this element.

The earliest observations of the spectra of metals which cannot be volatilized at the temperature of the non-luminous gas-flame were made in 1835 by Wheatstone. He allowed electric sparks to pass between poles of different metals, and found that the spectra of the sparks thus obtained were dissimilar. From this he concluded that the electric spark resulted from the volatilization of the metal of the poles. "These differences," he says, "are so obvious, that one metal may easily be distinguished from another by the appearance of its spark; and we here have a mode of discriminating metallic bodies more readily than that of chemical examination, and which may hereafter be employed for useful purposes."

In 1855 Ångström thoroughly investigated the nature of the electric spark, proving the important fact that the spark yields two superimposed spectra; one derived from the metal of the pole, and the other from the gas or air through which the spark passes.

The results obtained by the above-mentioned observers were, however, but little known, and the method was never applied to the solution of problems in analytical chemistry, until the year 1860, when Bunsen and Kirchhoff began their classical researches. It is to these two philosophers that we must in truth ascribe the discovery of the spectrum analytical method, for they were the first to bring to bear upon this subject the sound principles of modern research, and to establish it upon the firm foundation of exact experiment.[1] Their labours soon met with their reward. A new alkaline metal (cæsium) was almost immediately discovered,[2] and the presence of various well-known metals in the solar atmosphere was at the same time ascertained beyond doubt.[3]

[1] Kirchhoff and Bunsen, "Chemical Analysis by Spectrum Observations," Memoir I. *Phil. Mag.* [4], xx. 89; ditto, Memoir II. *Phil. Mag.* [4], xxii. 329, 498.
[2] *Berlin Acad. Ber.* May 10, 1860; *Chem. News*, iii. 132.
[3] *Berlin Acad. Ber.* Oct. 27, 1859; *Phil. Mag.* [4], xix. 193.

CONSTRUCTION AND USE OF THE SPECTROSCOPE.

673 The construction and arrangement of a spectroscope best suited to ordinary chemical purposes is shown in Fig. 176. This instrument consists of a prism (*a*) fixed upon a firm iron stand, and a tube (*b*) carrying the slit (*d*), seen on an enlarged scale in Fig. 178, through which the rays from the coloured flame (*e* and *e'*) fall upon the prism, being rendered parallel by passing through a lens. The light, having been refracted, is received by the telescope (*f*), and the image magnified before reaching

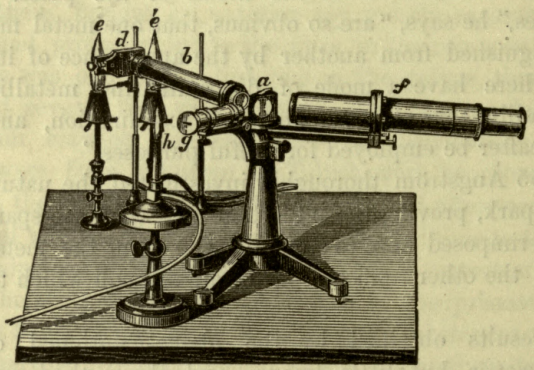


Fig. 176.

the eye. The rays from each flame are made to pass into the telescope (*f*); one set through the upper uncovered half of the

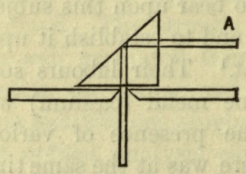


Fig. 177.

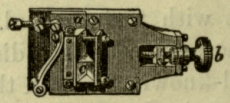


Fig. 178.

slit, the other by reflection from the sides of the small prism (*c* Figs. 177 and 178), through the lower half; thus bringing the two spectra into the field of view at once, so as to be able to make any wished-for comparison of the lines. The small

luminous gas-flame (*h*, Fig. 176) is placed so as to illuminate a fixed scale contained inside the tube (*g*); this is reflected from the surface of the prism (*a*) into the telescope, and serves as a means of measuring the position of the lines. The rays from one of the flames pass direct through the upper part of the slit, whilst those (A) from the other flame, placed on one side, are reflected (by total or internal reflection) from the surface of the prism through the lower part of the slit in the direction indicated by Fig. 177. The object of this superposition of the spectra is evident: it is to enable us to see whether the substance under examination really is the body which it is supposed to be. For instance, if we place a small quantity of the substance which we know to contain sodium in the one flame, and some of the substance to be tested in the other, and then, if the spectra of these two flames be sent into the telescope one above the other by means of a small reflecting prism placed on the end of the slit, we see at the same time the spectrum of the pure sodium and the spectrum supposed to be that of sodium; and we can readily observe whether the lines coincide. If they coincide, and the two spectra have these lines exactly continuous one below the other, then we are quite certain that sodium, or any other substance which we may have been investigating, is present.

An improvement has recently been made by the construction of spectroscopes provided with illumination-scales, which are divided and numbered so as to permit of the direct determination of the wave-length of any region of the visible spectrum.

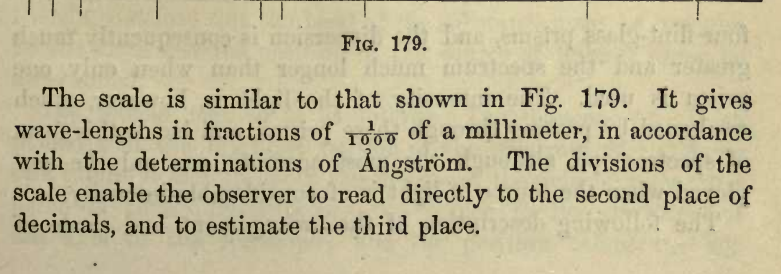


FIG. 179.

The scale is similar to that shown in Fig. 179. It gives wave-lengths in fractions of $\frac{1}{1000}$ of a millimeter, in accordance with the determinations of Ångström. The divisions of the scale enable the observer to read directly to the second place of decimals, and to estimate the third place.

Thus the wave-length of Fraunhofer's line E is, according to Ångström, 0 0005273 mm. or $\mu 0{\cdot}5273$. In an instrument made by Zeiss of Jena, the observer would at once see that the line was placed between division 52 and 53, and he would determine the fraction of the division to within one-tenth, but probably much nearer; the reading would probably be 52·7, which would give him the wave-length $\mu 0{\cdot}527$. As a result of many observations we have found that the mean error in the case of unexperienced observers is not greater than $\pm$ 0·000001 of a millimeter. In the regions of the spectrum with a lower wave-length than D the error is less.

674 Another and more complete form of spectroscope, used by Kirchhoff and especially adapted for physical research, is represented in Fig. 180. In this instrument the rays pass through

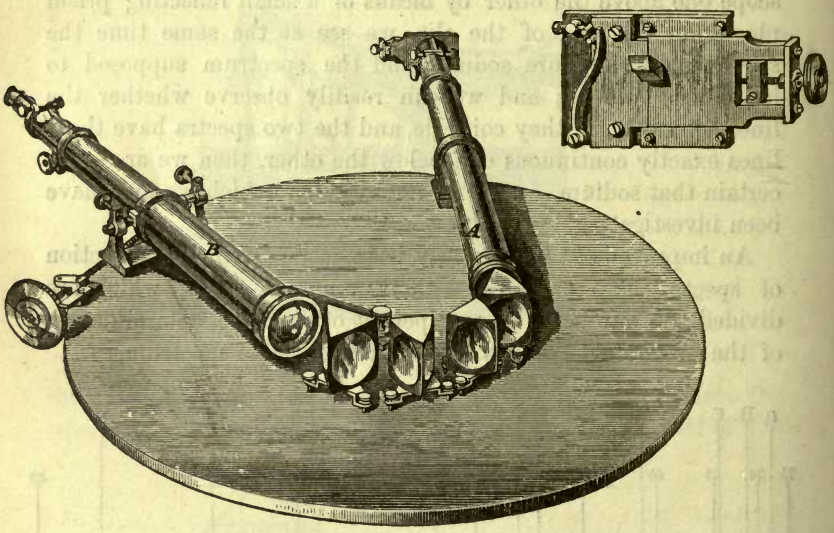


FIG. 180.

four flint-glass prisms, and the dispersion is consequently much greater and the spectrum much longer than when only one prism is used. The intensity of the light is, however, much weakened by passing through these prisms, and hence this form of spectroscope, although the most accurate, can only be employed when the source of light is of considerable intensity.

The following description of the arrangement and mode of

using the spectroscope is given by Bunsen and Kirchhoff:— The telescope (*f*) is first drawn out so far that a distant object is plainly seen, and screwed into the ring, in which it is held, care being taken to loosen the screws beforehand; the tube (*b*) is then brought into its place, and the axis of B brought into a straight line with that of (*b*). The slit is then drawn out until it is distinctly seen on looking through the telescope, and this latter is then fixed by moving the screws, so that the middle of the slit is seen in about the middle of the field of view. After removing the small spring, the prism is next placed on the brass plate, and fastened in the position which is marked for it, and secured by screwing down the spring. If the axis of the tube (*b*) be now directed towards a bright surface, such as the flame of a candle, the spectrum of the flame is seen in the lower half of the field of the telescope on moving the latter through a certain angle round the axis of the foot. When the telescope has been placed in position, the tube (*g*) is fastened on to the arm belonging to it, and this is turned through an angle round the axis of the foot, such that, when a light is allowed to fall on the divided scale, the image of the scale is seen through the telescope (*f*), reflected from the nearer face of the prism; this image is brought exactly into focus by altering the position of the scale in the tube (*g*); and by turning this tube on its axis it is easy to make the line in which one side of the division on the scale lies parallel with the line dividing the two spectra, and by means of the screw (*d*) to bring these two lines to coincide.

In order to bring the two sources of light (*e* and *e'*) into position, two methods may be employed. One of these depends upon the existence of bright lines in the inner cone of the colourless gas-flame, which have been so carefully examined by Swan. If the lamp (*e*) be pushed past the slit, a point is easily found at which these lines become visible; the lamp must then be pushed still further to the left, until these lines nearly or entirely disappear; the right mantle of the flame is now before the slit, and into this the bead of the substance must be brought. In the same way the position of the source of light (*e'*) may be ascertained.

The second method is as follows: The telescope (*f*) is so placed that the brightest portion of the spectrum of the flame of a candle is seen in about the middle of the field of view; the flame is then placed before the ocular in the direction of the axis of the telescope; and the position before the slit

determined in which the upper half of the slit appears to be the brightest; the lamp (*e*) is then placed so that the slit appears behind that portion of the flame from which the most light is given off after the introduction of the bead. In a similar way the position of the lamp (*e'*) is determined by looking through the small prism and the lower half of the slit.

By means of the screw the breadth of the slit can be regulated in accordance with the intensity of the light and the degree of purity of spectrum which is required. To cut off foreign light a black cloth, having a circular opening to admit the tube (*g*), is thrown over the prism (*a*) and the tubes (*b* and *f*). The illumination of the scale is effected by means of a luminous gas-flame placed before it; the light can, if necessary, be lessened by placing a silver paper screen close before the scale. The degree of illumination suited to the spectrum under examination can then be easily found by placing this flame at different distances.

SPECTRA OF GASES.

675 In order to obtain the peculiar spectrum of a chemical substance it is necessary that the light be examined which this substance emits in a state of glowing gas. The method which must be employed for this purpose differs according as the substance is solid, liquid, or gaseous. If the body be a gas at the ordinary temperature the gaseous particles can be made to glow, and then to emit the rays which are peculiar to them, by passing an electric discharge through them. The colour of

FIG. 181.

the electric spark or discharge will then be found to vary according to the nature of the gas, and an examination by means of a spectroscope of the light then emitted reveals the characteristic spectrum of the gas. The examination of the spectra of gases is best effected by means of *Geissler's Tubes* (Fig. 181). These contain the gases in a highly rarefied condition, and are

furnished with platinum or aluminium wires melted through the glass, and as the rarefied gases offer little resistance to the passage of the electricity, the discharge passes readily through a long narrow tube, heating up in its passage the particles of gas, and thus producing a column of brightly luminous gas. Liquids which are easily volatilized can also be examined in this way.

FLAME-SPECTRA.

676 Less volatile substances, such as the salts of the metals of the alkalis and alkaline earths, may be placed upon a fine platinum wire, and this then brought into the non-luminous flame. The salts there volatilize, the flame becomes tinged of a characteristic colour, and this coloured flame, when examined by the spectroscope, exhibits the peculiar spectrum of the given substance.

SPARK-SPECTRA.

677 Again, when the substance is non-volatile at the temperature of the non-luminous flame, as is the case with most metals, and requires a much higher temperature to convert it into gas, either a powerful electric spark or the electric arc must be

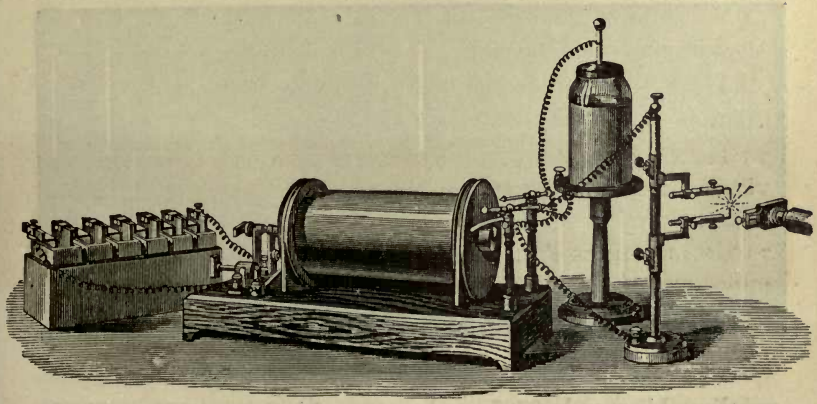


FIG. 182.

employed. The arrangement used for obtaining the spectra of metals by means of the electric spark is seen in Fig. 182. It is only necessary to allow a powerful and bright spark to

pass between poles made of the metal in question to obtain the characteristic bright-line spectrum of the metal, although it is to be remembered that the bright lines of the gases through which the spark passes (the air lines) will likewise be observed.

VARIATION OBSERVED IN SPECTRA.

678 If we compare the spectra of the various elements obtained according to one or other of the above methods, we find that each yields a characteristic spectrum, consisting of a larger or smaller number of bright lines. These lines do not undergo any alteration in relative position, or in degree of refrangibility, when the temperature is increased. The sodium double yellow line D is always seen at the same position of the spectrum, viz., wave-lengths 5895 and 5889, to whatever temperature the vapour may be raised. The *number* of lines visible in any given spectrum, as well as their relative intensities, may, on the contrary, undergo considerable changes dependent upon the temperature of the glowing gas, the pressure to which it is subjected, and the thickness of the incandescent layer. Thus, for example, the spectrum of lithium, as obtained by placing some salt of the metal in a non-luminous gas-flame, consists of one very bright

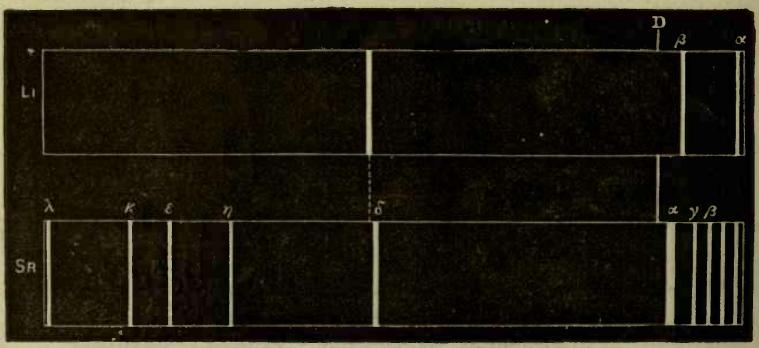


Fig. 183.

red line, Li. *a*, w. l. 6705, and a very faint orange line, Li. *β*, w. l. 6102. If, however, the spectrum of lithium, obtained by placing some of its salts in the electric arc, or even in the oxyhydrogen flame, be examined, a new and splendid blue line (Li. *γ*), having a wave-length of 4603, makes its appearance.

The same phenomenon is observed in the case of the strontium spectrum, where no less than four new lines (ϵ, η, κ, and λ, Fig. 183) make their appearance on increasing the temperature of the incandescent vapour of the metal.

In like manner hydrogen, when examined by the ordinary electric spark, or in an ordinary Geissler's tube, yields a spectrum which consists of four lines, viz.:

H α	coincident with	Fraunhofer's line	C	in the	red . . .	wave-length	6562.
H β	,,	,,	F	,,	bluish green	,,	4861.
H γ	,,	,,	G	,,	indigo . .	,,	4340.
H δ	,,	,,	h	,,	violet . .	,,	4101.

The lines H α, H β, and H γ are seen to be very bright when the gas is rarefied to a certain point; but if this rarefaction be carried on further the line H α gradually disappears, whilst H β, though fainter, remains well defined. If, on the other hand, the intensity of the spark is increased, the bands H β and H γ begin to broaden, and when the tension of the gas is increased to 360 mm., and a Leyden jar is introduced into the circuit, the bright lines are found to give way to a continuous spectrum.

Incandescent gas may, under certain conditions, emit a continuous spectrum. Kirchhoff has shown that when the temperature or density of a glowing gas is increased, and the luminosity of the spectrum becomes greater, the dark portions of the spectrum must increase in luminosity more rapidly than the bright portions. Hence it does not appear surprising that by increase of temperature and pressure the spectrum, originally consisting of bright lines or bands upon a scarcely visible continuous background, should by degrees change into a spectrum exhibiting all the colours in equal intensity.

Still we must remember that other explanations of the fact that gas gives a continuous spectrum may be found; and on the other hand many gases give continuous spectra when the temperature is lowered.

SPECTRA OF METALS AND NON-METALS.

679 The spectra of the non-metallic elements differ in several respects from those of the metals, to which latter class hydrogen, by virtue of its chemical relations, may be considered to belong. Metals yield spectra made up of well-defined sharp lines, the breadth of each of which is limited only by the breadth of the slit. These bright lines undergo no change of refrangibility

within wide variations of temperature. Such a spectrum is called a *line-spectrum*

The spectrum of a non-metal as obtained at comparatively low temperatures presents a totally different aspect. Instead of consisting of fine bright lines, it is made up of bright bands the breadth of which is independent of the breadth of the slit, and which often succeed each other in the spectrum in regular order. Hence these are termed *channelled-space* spectra.

Attempts have been made to classify the elements according to their emission spectra; that is, to draw a distinction between the spectra of the metals and those of the non-metallic elements, or even to group the metals according to their spectra. To a certain extent these attempts have been successful. Thus, for example, the compounds of sodium, potassium, lithium, calcium, and rubidium, when brought into the flame of a Bunsen burner exhibit their metallic spectra, so that the spectra of their chlorides or oxides have not been obtained, unless, indeed, one of the red bands of potassium may be due to the oxide, and this has not been satisfactorily proved. On the other hand, when the salts of calcium, barium, and strontium are brought into the flame only the brightest of the metallic lines are visible, whilst a strong spectrum of their oxides is seen. The spark of similar elements also show a certain similarity. Thus iron, cobalt, and nickel give spectra containing a great number of lines distributed in series of groups throughout the spectrum. Zinc and cadmium, on the other hand, show few lines, and these stand by themselves, and are not grouped together. These and other similarities have been pointed out at various times, but some of the conclusions must be received with caution, as the similarities in many cases are simply consequences of similar chemical properties of the metals in one group. Thus the fact that the alkalis give metallic spectra at the temperature of the flame, and that we cannot obtain the spectra of their haloid compounds, simply means that these metals are easily volatile, and that their haloid compounds are decomposed at a temperature below that of the flame. Calcium, barium, and strontium, being less volatile, and forming compounds which are more stable at high temperatures, chiefly exhibit the spectra of the oxide when thus treated.

Recent researches have however rather tended to destroy any sharp line of demarcation between the spectra of metals and non-metals, for although Plücker first observed a channelled-

space spectrum in the case of several metalloids, it has since been shown that the absorption spectra of very many metals consist of channelled spaces ; on the other hand, oxygen, except at the negative pole, gives no channelled-space spectrum, but a line-spectrum, whilst under the same circumstances the nitrogen spectrum consists of a channelled-space one. On the whole, however, it may be said that the channelled-space spectra of the metalloids are more stable and exist at higher temperatures than the channelled-space spectra of the metals. When the non-metallic element is heated much more strongly, this channelled-space spectrum is found to give place to a fine line-spectrum, and this does not undergo any further alteration upon increase of temperature. Thus sulphur, when it burns in the air or in oxygen gives rise to a continuous spectrum, but if a little sulphur be introduced into a Geissler's tube and the air withdrawn, a *band spectrum* is seen upon warming the tube and passing an electric discharge through it. On continuing to heat the tube the band spectrum changes to one of permanent bright lines.

SPECTRA OF COMPOUNDS.

680 Chemical compounds yield a third order of spectra. Certain chemical compounds can be volatilized in the non-luminous gas-flame without undergoing decomposition. Thus if a bead of calcium chloride be brought into the flame a reddish tint is

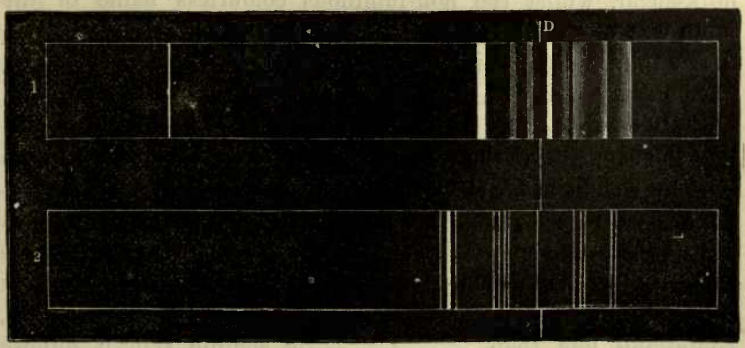


Fig. 184.

observed, caused by the volatilization of the salt. The spectrum of this coloured flame consists of a series of differently coloured road bands, whose position is indicated by No. 1, Fig. 184

If now, the same bead be placed between two metallic poles, and a bright electric spark be allowed to strike round the bead, the spark is seen to assume a bright-red tint, and when this coloured spark is observed by means of a spectroscope a spectrum of fine bright lines, shown in No. 2, Fig. 184, is seen. In the first instance the spectrum is that of an incandescent calcium compound; in the second it is that of the metal itself.

APPLICATION OF THE SPECTROSCOPE TO CHEMICAL ANALYSIS.

681 This instrument is especially valuable in the ordinary qualitative analysis for the detection of the metals of the alkalis and alkaline earths, and of the new metals thallium, indium, and gallium, inasmuch as the salts of the above metals can be volatilized in the non-luminous gas-flame. The following extract from Bunsen and Kirchhoff's memoir on this subject gives some idea of the ease and accuracy with which the presence of certain of these metals can be detected, and leads to the conclusion that sodium salts are universally distributed:

"The following experiment shows that the chemist possesses no reaction which in the slightest degree will bear comparison as regards delicacy with this spectrum analytical determination of sodium. In a far corner of our experiment room, the capacity of which was about sixty cubic meters, we burnt a mixture of three milligrams of chlorate of sodium with milk-sugar, whilst the non-luminous colourless flame of the lamp was observed through the slit of the telescope. Within a few minutes the flame, which gradually became pale yellow, gave a distinct sodium line, which, after lasting for ten minutes, entirely disappeared. From the weight of sodium salt burned and the capacity of the room, it is easy to calculate that in one part by weight of air there is suspended less than $\frac{1}{20.000.000.000}$ of a part of soda smoke. As the reaction can be observed with all possible comfort in one second, and as in this time the quantity of air, which is heated to ignition by the flame, is found to be only about 50 cub. cent. or 0·0647 grm. of air, containing less than $\frac{1}{20.000.000.000}$ of sodium salt, it follows that the eye is able to detect with the greatest ease quantities of sodium salt less than $\frac{1}{3.000.000}$ of a milligram in weight. With a reaction so delicate, it is easy to understand why a sodium reaction is almost always noticed in ignited atmospheric

air. More than two-thirds of the earth's surface is covered with a solution of chloride of sodium, fine particles of which are continually being carried into the air by the action of the waves. These particles of sea-water cast thus into the atmosphere evaporate, leaving almost inconceivably small residues, which floating about, are almost always present in the air, and are rendered evident to our eyes in the sunbeams. These minute particles perhaps serve to supply the smaller organized bodies with the salt which larger animals and plants obtain from the ground. In another point of view, however, the presence of this chloride of sodium is of interest. If, as is scarcely doubtful at the present time, the explanation of the spread of contagious disease is to be sought for in some peculiar contact action, it is possible that the presence of so antiseptic a substance as chloride of sodium, even in almost infinitely small quantities, may not be without influence upon such occurrences in the atmosphere.

"By means of daily and long-continued spectrum observations, it would be easy to discover whether the alterations of intensity in the line Naα produced by the sodium in the air have any connection with the appearance and the direction of march of an epidemic disease.

"The unexampled delicacy of the sodium reaction explains also the well-observed fact, that all bodies after a lengthened exposure to the air show the sodium line when brought into a flame, and that it is only possible in a few salts to get rid of the line even after repeated crystallization from water which had only been in contact with platinum. A thin platinum wire freed from every trace of sodium salt by ignition, shows the reaction most visibly on allowing it to stand for a few hours in the air; in the same way the dust which settles from the air in a room shows the bright line Naα. To render this evident it is only necessary to knock a dusty book, for instance, at a distance some feet from the flame, when a wonderfully bright flash of yellow band is seen."

In like manner the metal lithium before the year 1860 was known only to exist in a few rare minerals. It is now ascertained that lithium compounds are most widely distributed, occurring not only in every mineral spring, but in river- and sea-water, in the juices of almost every plant, and even in human blood and muscular tissue.

682 Again, to quote from Bunsen's Memoir: "Minerals containing lithium, such as triphylline, triphane, petalite, and lepidolite

require only to be held in the flame in order to obtain the bright line in the most satisfactory manner. In this way the presence of lithium in many felspars can be directly detected; as, for instance, in the orthoclase from Baveno. The line is only seen for a few moments, directly after the mineral is brought into the flame. In the same way the mica from Altenburg and Penig was found to contain lithium, whereas micas from Miask, Aschaffenburg, Modum, Bengal, Pennsylvania, &c., were found to be free from this metal. In natural silicates which contain only small traces of lithium this metal is not observed so readily. The examination is best conducted as follows: A small portion of the substance is digested and evaporated with hydrofluoric acid or fluoride of ammonium, the residue moistened with sulphuric acid and heated, the dry mass being dissolved in absolute alcohol. The alcoholic extract is then evaporated, the dried mass again dissolved in alcohol, and the extract allowed to evaporate on a shallow glass dish. The solid pellicle which remains is scraped off with a fine knife, and brought into the flame by the thin platinum wire. For one experiment $\frac{1}{10}$th of a milligram is in general quite a sufficient quantity. Other compounds besides the silicates, in which small traces of lithium require to be detected, are transformed into sulphates by evaporation with sulphuric acid or otherwise, and then treated in the manner described.

"In this way we arrive at the unexpected conclusion that lithium is most widely distributed throughout nature, occurring in almost all bodies. Lithium was easily detected in forty cubic centimeters of water of the Atlantic Ocean, collected in 41° 41′ N. latitude and 39° 14′ W. longitude.

"Ashes of marine plants (kelp) driven by the Gulf Stream on to the Scotch coasts contain evident traces of this metal. All the orthoclase and quartz from the granite of the Odenwald which we have examined contain lithium. A very pure spring water from the granite in Schleierbach, on the west side of the valley of the Neckar, was found to contain lithium, whereas the water from the red sandstone which supplies the Heidelberg laboratory was shown to contain none of this metal. Mineral waters, in a liter of which lithium could hardly be detected according to the ordinary methods of analysis, gave the line Li*α* even if only a drop of the water on a platinum wire was brought into the flame. All the ashes of plants growing in the

Odenwald on a granite soil as well as Russian and other potashes contain lithium.

"Even in the ashes of tobacco, in vine-leaves, in the wood of the vine and in the grapes, as well as in the ashes of the crops grown on the Rhine plains near Wäghausel, Deidesheim, and Heidelberg, on a non-granite soil, was lithium found. The milk of the animals fed on these crops also contains this widely diffused metal."

The special details of the spectra of the metals of the alkalis and alkaline earths will be found under the description of each metal.

683 The following graphic description of the phenomena observed when a small quantity of the mixed salts of the above metals is brought into the non-luminous flame is from the pen of Professor Bunsen:

"A mixture of the chlorides of potassium, sodium, lithium calcium, strontium, and barium, containing at the most $\frac{1}{10}$th of a milligram of each of these salts, was brought into the flame, and the spectra produced were observed. At first the bright yellow sodium line, Naα, appeared with a background formed by a nearly continuous pale spectrum: as soon as this line began to fade, the exactly defined red line of lithium, Li α, was seen, and still further removed from the sodium line the faint red potassium line, Kaα, was noticed; whilst the two barium lines, Baα, and Baβ, with their peculiar form became visible in the proper position. As the potassium, sodium, lithium, and barium volatilized, their spectra became fainter and fainter, and their peculiar bands one after the other vanished, until, after the lapse of a few minutes, the lines Caα, Caβ, Srα, Srβ, Srγ, Srδ, became gradually visible, and, like a dissolving view, at last attained their characteristic distinctness, colouring, and position, and then, after some time, became pale and disappeared entirely. The absence of any one, or of several of these bodies, is at once indicated by the non-appearance of the corresponding bright lines.

"Those who become acquainted with the various spectra by repeated observation do not need to have before them an exact measurement of the single lines, in order to be able to detect the presence of the various constituents: the colour, relative position, peculiar form, variety of shade, and brightness of the bands are quite characteristic enough to ensure exact results even in the hands of persons unaccustomed to such work. These

special distinctions may be compared with the differences of outward appearance presented by the various precipitates which we employ for detecting substances in the wet way. Just as it holds good as a character of a precipitate that it is gelatinous, pulverulent, flocculent, granular, or crystalline, so the lines of the spectrum exhibit their peculiar aspects, some appearing sharply-defined at their edges, others blending off either at one side or both sides, either similarly or dissimilarly; or some, again, appearing broader, others narrower; and, just as in ordinary analysis, we only make use of those precipitates which are produced with the smallest possible quantity of the substance supposed to be present, so in analysis with the spectrum, we employ only those lines which are produced by the smallest possible quantity of the substance, and require a moderately high temperature. In these respects both analytical methods stand on an equal footing; but analysis with the spectrum possesses a great advantage over all other methods, inasmuch as the characteristic differences of colour of the lines serve as the distinguishing feature of the system. Most of the precipitates which are valuable as reactions are colourless; and the tint of those which are coloured varies very considerably, according to the state of division and mechanical arrangement of the particles. The presence of even the smallest quantity of impurity is often sufficient entirely to destroy the characteristic colour of a precipitate; so that no reliance can be placed upon nice distinctions of colour as an ordinary chemical test. In spectrum analysis, on the contrary, the coloured bands are unaffected by such alterations of physical conditions, or by the presence of other bodies. The positions which the lines occupy in the spectrum give rise to chemical properties as unalterable as the combining weights themselves, and which can therefore be estimated with an almost astronomical precision. The fact, however, which gives to this method of spectrum analysis an extraordinary importance is, that the chemical reactions of matter thus reach a degree of delicacy which is almost inconceivable. By an application of this method to geological inquiries concerning the distribution and arrangement already mentioned, we are led to the unexpected conclusion that not only potassium and sodium, but also lithium and strontium, must be added to the list of bodies occurring only indeed in small quantities, but most widely spread throughout the matter composing the solid body of our planet.

"The method of spectrum analysis may also play a no less important part as a means of detecting new elementary substances; for if bodies should exist in nature so sparingly diffused that the analytical methods hitherto applicable have not succeeded in detecting or separating them, it is very possible that their presence may be revealed by a simple examination of the spectra produced by their flames. We have had opportunity of satisfying ourselves that in reality such unknown elements exist. We believe that, relying upon unmistakeable results of the spectrum analysis, we are already justified in positively stating that besides potassium, sodium, and lithium, the group of the alkaline metals contains a fourth member which gives a spectrum as simple and characteristic as that of lithium, a metal which in our apparatus gives only two lines, namely, a faint blue one, almost coincident with the strontium line Srδ, and a second blue one lying a little further towards the violet end of the spectrum, and rivalling the lithium line in brightness and distinctness of outline."

684 *Cæsium and Rubidium.* The discovery by Bunsen of a second new alkaline metal found in the mineral water of Durkheim,[1] soon followed that of the first. Both of these new elements are contained in the mineral water in extremely small quantities, so that 44,000 kilos. of the water had to be evaporated in order to obtain 16·5 grams of the mixed chlorides. The first of these new metals yields a spectrum distinguished by two splendid bright blue lines, and hence the name *Cæsium* (*cæsius*, the blue colour of the sky) was given to it. The second new metal is characterised by a spectrum which contains a bright red line less refrangible than the potassium line Kα, and also a line in the violet. As the red line is the one by which the presence of this metal can be most readily and certainly detected, Bunsen gave to it the name of *Rubidium* (*rubidus*, dark-red).

Since the discovery of these two bodies by Bunsen in 1860, chemists have recognised the presence of both these metals in very varied situations; one of them, rubidium, being comparatively widely distributed, and found in very many mineral waters. Thus, for example, the celebrated waters of Bourbonne-les-Bains contains 0·032 grm. of chloride of cæsium, and 0·010 grm. of chloride of rubidium in one liter of water; whilst in the well-known springs of Vichy, Gastein, Nauheim, Karlsbrunn, and many more, either one or both of these new metals have been discovered. Rubidium has been found to be

[1] An analysis of this water is found at p. 249 of Vol. I.

still more widely diffused than cæsium, occurring both in animate as well as in inanimate nature. It has been found in beetroot, in tobacco, in the ash of the oak (the *Quercus pubescens*), in coffee, in tea, and in cocoa. In their general chemical characters, as in their spectroscopic relations, these two new metals exhibit the closest analogy with potassium. So much so is this the case, that without the aid of the spectroscope and the differences which the spectra of these three metals present, it was absolutely impossible to distinguish between them. Chemists had, in fact, experimented upon cæsium but had mistaken it for potassium.

A rare mineral called *Pollux* occurs in the island of Elba, This mineral was analyzed in the year 1846 by the well-known chemist Plattner, and by him it was supposed to contain potassium. In calculating out the results of his analysis, Plattner invariably found a considerable loss, the cause of which he was unable to account for. Spectrum analysis has now explained this anomaly, for since the discovery of the two new metals it has been found that it was not potassium, but the new metal cæsium, which was present, of the oxide of which no less than 34 per cent. is contained in this mineral. The want of agreement of the former analysis is wholly attributable to the difference of the combining weight of these two bodies, that of potassium being only 39 1, whilst that of cæsium is 133: and if this last number be used the analyses calculate, as they ought to do, exactly to 100 parts. (Vol. II. Part I. p. 169.)

Soon after the discovery of the new alkaline metals by Bunsen, Mr. Crookes, in 1861, proved the presence of a third new metal in a seleniferous deposit from a sulphuric acid chamber at Tilkerode in the Harz. To this new element he gave the name of *Thallium*, from *thallus*, a young twig, owing to the bright green colour which this substance and its compounds impart to the non-luminous flame. The spectrum of thallium is a simple one, consisting of one bright green band (Tl *a*), having a wave-length of 5,349 ten-millionths of a millimeter. Thallium has since been shown to be frequently contained in iron-pyrites and several other minerals, so that it is a somewhat widely-distributed element. It exhibits very remarkable and interesting chemical properties. In certain respects it closely resembles the metals of the alkalis. In others it more nearly approaches the heavy metal lead. Hence thallium has very appropriately been termed by Dumas the ornithorhynchus amongst the metals. (Vol. II. Part I. p. 300.)

A fourth new metal was discovered in the year 1864, by Reich and Richter, in Freiberg. They gave to this substance the name of *Indium*, owing to the fact that it imparts a dark-blue or indigo tint to the flame, and its spectrum consists of two indigo-coloured lines. It has been found, although in small quantities only, in the zinc-blendes from Freiberg, Goslar, and a few other places (Vol. II. Part I. p. 499).

In 1875 a French chemist, Lecoq de Boisbaudran, found a fifth new metal in zinc-blendes from the Pyrenees. To this substance he gave the name of *Gallium* (Vol. II. Part I. p. 502). Its spectra consists of two violet lines, which are best seen in the electric spectrum. The brightest of these lines has a wave-length of 4170; the second line, which is fainter, having a wave-length of 4040.

MAPPING SPECTRA.

685 The following method of mapping spectra has been proposed by Bunsen, and by this means persons unacquainted with the special appearances of individual spectra may soon learn to recognize the individual metals. "For the purpose of facilitating the numerical comparison of the data of various spectrum observations, we give in Fig. 185 graphical representations of the observations which are taken from the guiding lines given in the chromo-lithograph drawings of the spectra published in our former memoirs, and in which the prism was placed at the angle of minimum deviation. The ordinate edges of the small blackened surfaces, referred to the divisions of the scale as abscissæ, represent the intensity of the several lines, with their characteristic gradations of shade. These drawings were made when the slit was so broad and the flame of such a temperature, that the fine bright line upon the broad Ca *a* band began to be distinctly visible.

"This breadth of the slit was equal to the fortieth part of the distance between the sodium line and the lithium line *a*. For the sake of perspicuity, the continuous spectra which some bodies exhibit are specially represented on the upper edge of the scale, to the divisions of which they are referred as abscissæ. In order to render these drawings, which have reference to our instrument, applicable to observations upon the scale of any other apparatus which we may call B, it is only necessary to prepare a reduced scale, which is laid upon the several drawings and used in place

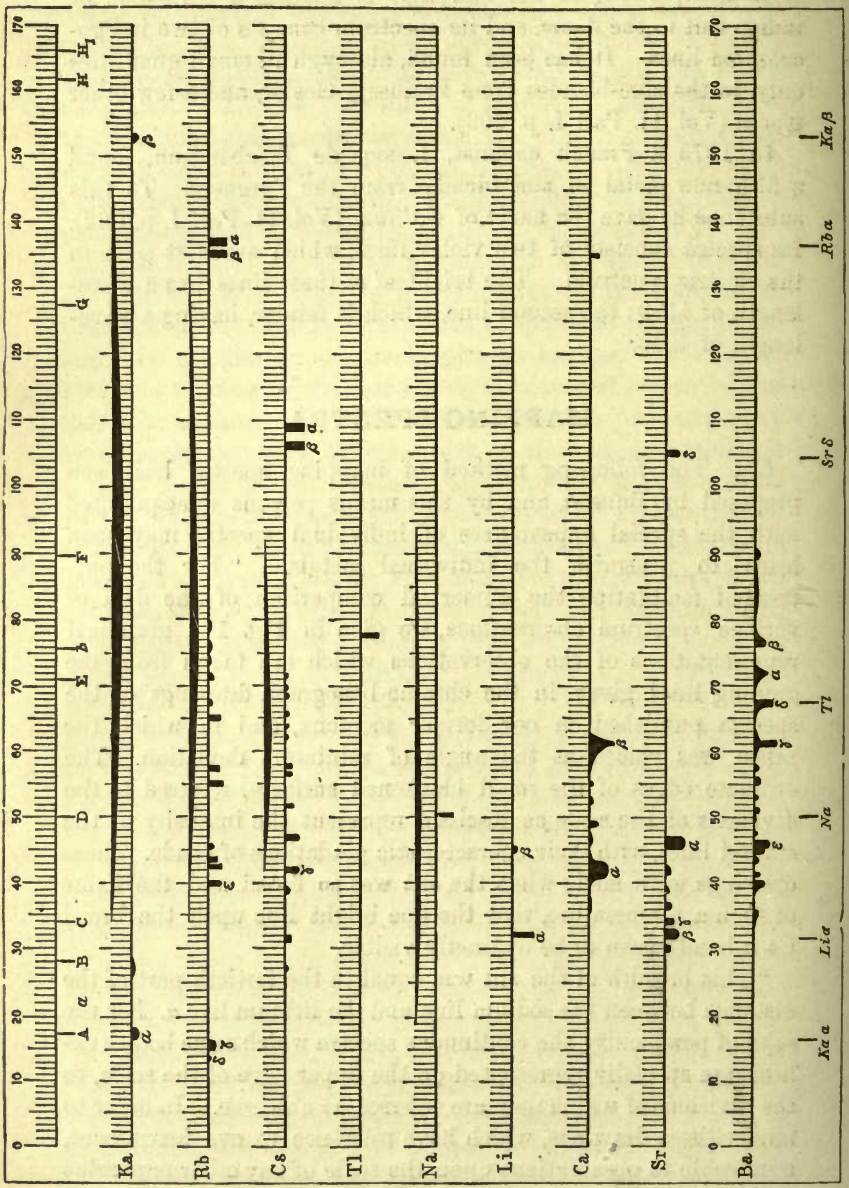


FIG. 185.

of the divided scale given in the figure. The lines marked at the bottom of Fig. 185 serve for the preparation of this new scale: these lines denote the distances between the lines Kα, Li α, Na, Tl, Sr δ, Rb α, and K β, measured according to the scale of our instrument. The position of each of these lines is determined by the edge of the line, which does not change its place on altering the breadth of the slit. The position of these same lines is read off on the scale of the instrument B, and the corresponding number written under each. A series of fixed points on the scale is thus obtained, and the complete divisions for the scale of instrument B is got by interpolating the values of the portions of the scale situated between the fixed points.

"The sodium line is then inserted in this scale, which is pasted upon a straight-edge, and the divisions numbered in tens and fives. If this measure be now laid down upon any of the drawings, so that the sodium line on the measure coincides with the division 50 on the drawing, the scale on the measure will give the position of all the lines in the particular spectrum exactly as they are seen in the photographic scale of the instrument B. When the position of the line under observation has in this way been ascertained, it is easy to assure oneself of its exact identity by means of the small prism on the slit of the spectroscope."

SPECTRA OF THE ELECTRIC SPARK.

686 By far the greater number of the metals, as well as a few of the non-metals, are vaporized at temperatures which can only be reached by the electric spark.

In order to facilitate the examination of such spark-spectra with especial regard to the easy chemical detection of these difficultly volatile metals, Bunsen[1] has proposed a special method.

The spark passes between two small cones of pure porous carbon, these having been impregnated with a solution of a chemically pure compound of the metal under examination. The advantages of this spark-spectrum method is well shown in the case of the detection of the rare allied metals, cerium, lanthanum and didymium; yttrium and erbium. The chlorides of these metals do not volatilize at the temperature of the non-luminous flame, but yield well-defined and characteristic spark-spectra by which they can, without difficulty, be recognized.

[1] *Phil. Mag.* [4], l. 418, 527.

PHOTOGRAPHING SPECTRA.

687 The most accurate mode of mapping and recognizing the spectra of the metals is that adopted by Lockyer. For this purpose photography has been called into play, the bright lines of each metal leaving their own picture on a sensitive collodion plate, which is placed on the apparatus in place of the eyepiece of the telescope. The image of the electric arc formed by the incandescence of the metal vaporized by means of thirty Grove's cells is projected by a lens on the slit of the spectroscope.

By this process Lockyer was enabled in the first place to confront the spectra of different metals with each other, and thus to eliminate coincident lines due to some common impurity contained in the various metals under examination. He was also able to examine the spectrum of various portions of the arc, and was thus led to the remarkable discovery that in each metallic spectrum certain lines are not only brighter and more intense than others, but are also *longer* than the rest. That is, that one line of a given metal is seen to stretch across from pole to pole, whilst another line only appears in the neighbourhood of the poles where the temperature is highest, and the density of the incandescent gas might be supposed to be greatest. These longest lines in the spectrum of a metal are always constant in position, so that if we know in what part of the spectrum to look for the brightest line of any metal, say of iron, and if we notice its presence, we need no longer trouble ourselves to search for other iron lines, but may be certain that iron is there. If, on the other hand, we do not see this longest and brightest line, we may with safety conclude that none of the other and less brilliant lines of the metal will be found. Working by the light of this discovery, Lockyer has come to the conclusion that most, if not all, of the cases of supposed coincidence between the lines of different metals are to be explained by the presence of an impurity common to both, which is in such minute quantity that it had eluded every other means of detection.

The great advantage which this photographic mode of record offers is, that it is possible thus to determine, with absolute accuracy, the positions of a very much greater number of lines than can be done by mere eye observation. This is shown by the fact that in the portion of the spectrum from wave-lengths 3,900 to 4,100 the number of lines of twelve metals noted by Lockyer is 416, as against thirty-nine lines observed by Thalén.

Photographing the Ultra-red portion. Under certain circumstances a film of silver bromide becomes sensitive to the red rays, and thus Captain Abney has proved that it is possible to obtain photographs not only of the visible yellow and red portion of the solar spectrum, but even of the portion invisible to our eyes. Maps have thus been obtained by Abney of the lines in the solar spectrum extending from wave-length 7,600 to wave-length 12,500.

ABSORPTION-SPECTRA.

688 In accordance with the important optical law known as the law of exchanges, every incandescent body is capable of absorbing, at the same temperature, exactly those kinds of rays which it emits. Hence a glowing body which yields a continuous spectrum exhibits, at the same temperature, a

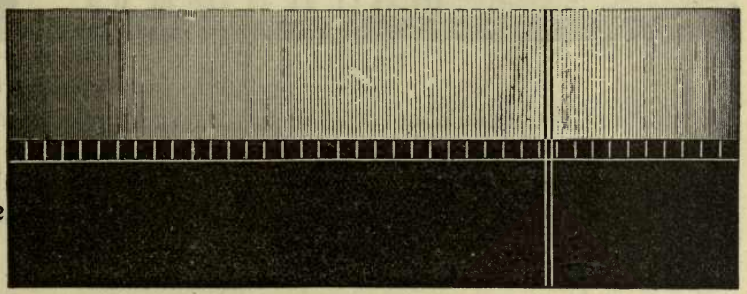


FIG. 186.

continuous absorption, whilst those bodies whose emission-spectra are broken or discontinuous, yield, under similar conditions of temperature, absorption-spectra which are in like manner broken or discontinuous. This selective absorptive action of glowing gases is strikingly shown in the case of sodium vapour. If a small piece of this metal be burnt in an iron cup in front of the slit of the spectroscope the bright yellow sodium lines will at first be seen, but they will soon be replaced by two dark lines which are exactly coincident with the bright yellow lines, and are seen upon a background of a bright continuous spectrum. The sodium spectrum has thus been *reversed*, inasmuch as the yellow rays in passing through the sodium vapour have been absorbed, whilst the particles of glowing oxide of the metal yield a continuous spectrum. Sodium vapour is opaque to the yellow D rays. In a similar way the bright

lines of the emission-spectra of lithium, calcium, strontium, barium, as well as of magnesium, copper, and several other heavy metals, have been reversed, or the absorption-spectra of these metals have been obtained. The numerous fine black lines seen in the solar spectrum and known as *Fraunhofer's lines*, are produced by the reversal of the spectra of hydrogen, sodium,

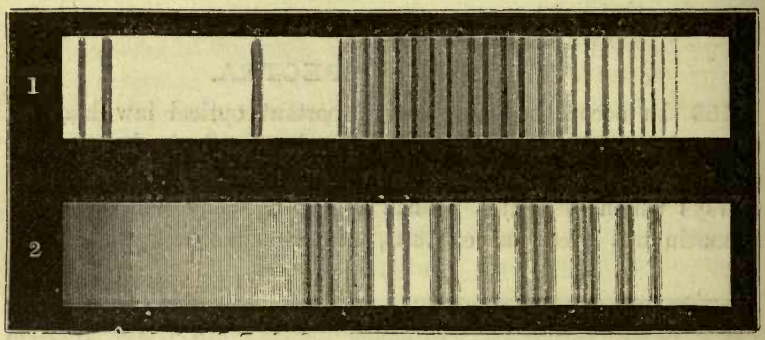


FIG. 187.

calcium, iron, magnesium, and other metals which are present in the state of luminous gas in the solar atmosphere.

This selective absorption is exhibited by certain liquid and solid bodies, as well as by gases, at the ordinary temperature of

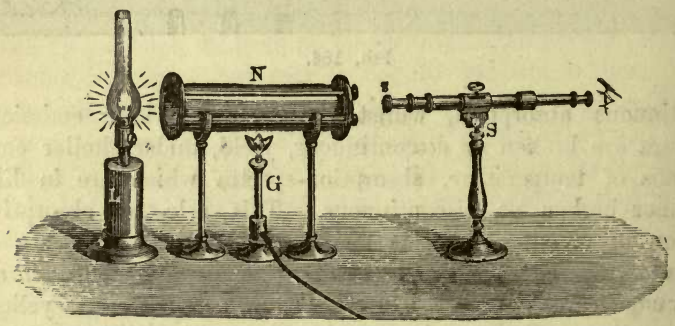


FIG. 188.

the air, and this property serves as a means of detecting the presence of the substances in question. The dark absorption bands seen when white light passes through the vapour of iodine (No. 1, Fig. 187) and those first observed by Brewster in the red flame of nitrogen peroxide (No. 2, Fig. 187), are good examples of this selective absorptive power of gases.

The arrangement shown in Fig. 188 is one which may be used for examining the absorption-spectra of gases by means of a direct-vision spectroscope. Even some colourless gases, such as aqueous vapour, possess a strong power of selective absorption when a column of sufficient depth is examined.

It has recently been shown that when we examine the absorption-spectra of two gases having the same density and colour, such as bromine and iodine monochloride, we find that, although their spectra present a general analogy, they are not identical. The absorption-spectra of the vapours of potassium and sodium have also been lately mapped. The absorption-spectrum of a substance is not, as a rule, identical with the emission-spectrum of the same body when examined at a lower temperature than that at which the bright line spectrum is obtained. Thus the dark absorption bands seen in iodine vapour are not identical with, or even analogous to, the bright lines of the emission-spectrum of iodine. This indicates that in the one case we have to do with a molecular condition different from that existing in the other case.

One of the most striking cases of absorption in the case of liquids is seen in solutions of salts of the metal didymium. All these nearly colourless salts possess the power of absorbing certain rays, so that if a small glass trough filled with a very dilute solution of a didymium salt be placed in front of the slit of the spectroscope and diffuse day-light or the light from a luminous gas-flame be allowed to pass through the solution into the spectroscope, two dark bands are seen on the luminous continuous spectrum. These lines are so characteristic and are produced by so small a quantity of didymium salt that this reaction serves as the most delicate as well as the most easy test for the presence of this metal.

Many coloured metallic solutions, such as chromium salts, permanganates, and uranium compounds, exhibit similar powers of selective absorption, and the bands thus produced may serve as a means of detection of the substances in question. Nevertheless the chemist is bound to use circumspection in arguing from the mere inspection of absorption-spectra, for these are by no means so certain or unfailing in their indications as the unaltering bright lines of the emission-spectra. This conclusion is borne out by the experiments of Bunsen on the didymium spectra. He has shown that the various compounds of this metal do not exhibit exactly the same absorption bands, and

that the crystallographic direction in which the ray of light passes through a crystal of a didymium salt exerts a marked influence on the arrangement of the dark bands.

Metallic solutions are not the only liquids which exhibit this power of selective absorption. Many organic liquids possess this power in a high degree, and by this means many complicated liquids of animal and vegetable origin can be easily distinguished when no other method can be employed. As an example of selective absorption in organic liquids, the spectrum reaction of the blood may be cited. No. 1, Fig. 189, exhibits the two dark bands, situated between Fraunhofer's D and E, seen

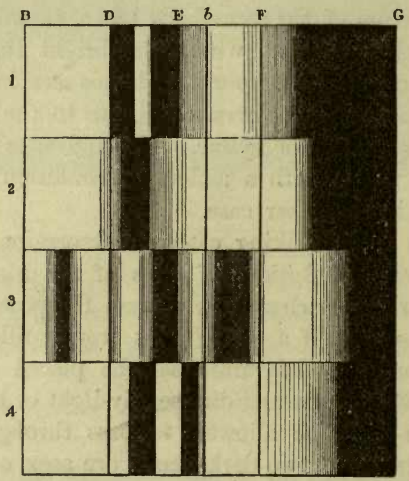


FIG. 189.

in oxidized blood and due to oxyhæmoglobin. No. 2 on the same figure shows the absorption-spectrum of deoxidized or venous blood, consisting of one dark band. By the action of an acid on blood the oxyhæmoglobin is converted into hæmatin yielding a different absorption-spectrum. The hæmatin, like the oxyhæmoglobin, is capable of undergoing oxidation and reduction. The absorption bands of hæmatin are shown in Nos. 3 and 4, Fig. 189. Another interesting fact with regard to blood-spectra is that the blood when it contains very small quantities of carbon monoxide in solution exhibits a very peculiar set of absorption bands. Carbon monoxide acts, however, as a very violent poison, and these peculiar bands are seen in the blood of animals which have been suffocated in the

fumes of burning charcoal. In the same way the peculiar compound which hæmogoblin forms with hydrocyanic acid yields a characteristic absorption-spectrum. The instrument with which these absorption-spectra can be observed with extremely small quantities of the liquids is a spectroscope placed in connection with a microscope. Fig. 190 shows the construction of such an instrument. The eyepiece contains prisms so arranged that the refracted rays pass in a straight line from the object into the eye. Such spectroscopes are termed direct-vision instruments, and are very portable and useful forms of the apparatus. This instrument, in the hands of Mr. Sorby, has proved capable of detecting $\frac{1}{1000}$ part of a grain of blood in a blood-stain.

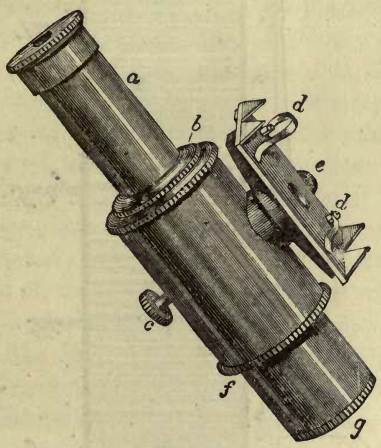


FIG. 190.

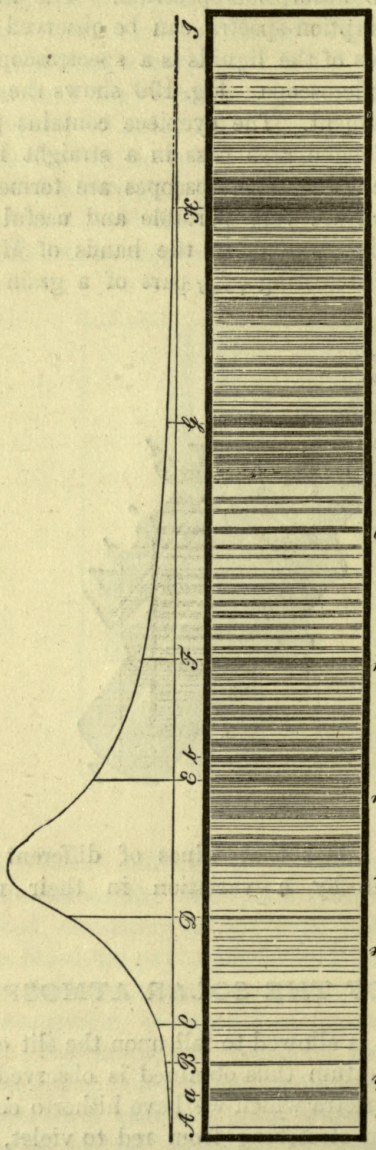
The same observer states that wines of different vintages may be distinguished by a variation in their respective absorption-spectra.[1]

COMPOSITION OF THE SOLAR ATMOSPHERE.

689 When sunlight is allowed to fall upon the slit of a spectroscope, the solar spectrum thus obtained is observed to differ essentially from the spectra which we have hitherto considered. A bright band is seen stretching from red to violet, but this band is cut up by a very large number of fine black lines. These lines are always present, and always occupy the same

[1] *Chem. News.* 1869, p. 295.

relative position in the solar spectrum—they are, in fact, shadows in the sunlight. They were first noticed by Wollaston, but first



carefully mapped by Fraunhofer, the principal lines being designated by him with the letters of the alphabet. Fig. 191 is a reduced facsimile of Fraunhofer's original map.

690 The cause of these dark solar lines was long a mystery. Fraunhofer finding that sunlight, both direct, and reflected as moonlight, always gave the same lines, whereas the light of the fixed stars contained different dark lines, came to the conclusion in 1814 that these dark lines were produced in the solar atmosphere, and not by the light passing through the intervening space, or through our own atmosphere.

It was not until the year 1860 that the true cause of the production of these lines was first clearly proved by Kirchhoff, not, however, before the same cause had been suggested as a possibility by Stokes. Kirchhoff was engaged in the comparison of the bright lines of certain metallic spectra with the dark lines in the sun. To his astonishment he found that *all* the bright lines of such metals as iron, calcium, and magnesium have dark representatives in the solar spectrum. Not only has each bright metal line a dark one coincident with it, but the breadth and intensity of the bright metal line is as a rule reproduced in the dark line in the solar spectrum, so that if a solar and a metal spectrum be allowed to fall one below the other in the field of the telescope, *all* the bright lines of the metal are seen to be coincident with the dark lines. Other metals, such for instance as gold and antimony, exhibit no such coincidences. Not one single bright line of these is found coincident with a dark solar line. Hence it is clear that there must be some kind of connection between the bright lines of these metals and the dark solar lines. Such coincidences cannot possibly be the result of mere chance. The coincidence of the *dark* solar lines with the *bright* iron lines is caused by the presence of iron in the sun's atmosphere.

We have already seen that the spectrum of sodium can be reversed. By passing the light from incandescent sodium through the vapour of the metal the bright yellow double line is changed to a dark one. If the solar atmosphere contains the vapours of sodium, of iron, of magnesium, of calcium, &c., in the state of glowing gas, and if white light from the incandescent mass beneath pass through these vapours, the effect produced would be exactly that which is in fact observed.

"As this is the only assignable cause, the supposition appears to be a necessary one. These iron vapours might be contained either in the atmosphere of the sun or in that of the earth. But it is not easy to understand how our atmosphere can contain such a quantity of iron vapour as would produce

the very distinct absorption-lines which we see in the solar spectrum; and this supposition is rendered still less probable by the fact that these lines do not appreciably alter when the sun approaches the horizon. It does not, on the other hand, seem at all unlikely, owing to the high temperature which we must suppose the sun's atmosphere to possess, that such vapours should be present in it. Hence the observations of the solar spectrum appears to me to prove the presence of iron vapour in the solar atmosphere with as great a degree of certainty as we can attain in any question of physical science" (Kirchhoff).

By observing the coincidences of these dark lines with the bright lines of terrestrial metals, we arrive at a knowledge of the occurrence of such metals in the solar atmosphere. The metals whose existence in the sun has now been ascertained, thanks to the labours of Kirchhoff, Angström, Thalén, and Lockyer, are the following:

Metals contained in the Sun's Atmosphere.

Hydrogen.	Magnesium.	Calcium.
Aluminium.	Sodium.	Titanium.
Barium.	Strontium.	Iron.
Manganese.	Nickel.	Cobalt.
Cerium.	Uranium.	Potassium.
Cadmium.	Zinc.	Chromium.
Lead.	Copper.	Bismuth.
Cæsium.	Beryllium.	Iridium.
Lanthanum.	Lithium.	Molybdenum.
Palladium.	Rubidium.	Tin.
Vanadium.	Yttrium.	

STELLAR SPECTRA.

691 In a similar way Drs. W. Allen Miller and Huggins have succeeded in proving that the elements hydrogen, sodium, calcium, magnesium, iron, bismuth, tellurium, antimony, and mercury occur in the atmosphere of the star Aldebaran, whilst other stars have been shown to contain other elements. More recently Dr. Huggins has applied the photographic mode of record to the spectra of stars, and has obtained permanent pictures of the dark lines in the stellar spectra drawn by nature itself.

From the observations of Secchi, the fixed stars may be divided into four groups, according to the different characters which their spectra present. The spectra of the first group exhibit merely four dark lines coincident with the bright lines of hydrogen. The white stars are those which belong to this group, such as Sirius and Vega. The second group contains the yellow stars, such as Pollux, Capella, &c. The spectra of these exhibit not only the hydrogen lines, but also those of several metals, and we may hence conclude that these stars possess a constitution similar to that of our sun. The red and blue stars, forming the third group, yield channelled-space spectra, which would lead to the conclusion that their atmospheres do not contain the glowing vapours of metals, but rather those of non-metallic elements, or possibly of certain chemical compounds. Such stars are Betelgeux and Hercules. The fourth and last group of stars gives a spectrum consisting of three bright bands, whose intensity is greatest towards the violet end of the spectrum.

The simpler a spectrum is, the simpler must be the composition of the body which yields that spectrum. Argueing upon these premises, Lockyer concludes that the atmospheres of the whiter stars contain the fewer elements and those of smaller atomic weight, and that as the peculiar colour of the star becomes more distinct its atmosphere becomes more complicated. These results, coupled with the well-known fact that dissociation of chemical compounds uniformly takes place if the temperature be only sufficiently high, has led Mr. Lockyer to suggest that the heat being greatest in the whitish stars, its simple spectrum can be best explained by the existence of a temperature sufficient to dissociate the substances to which on this earth we give the name of elementary bodies.

692 A very remarkable observation was made in May, 1866. A star which had hitherto been one of very small magnitude, known as T Coronæ, suddenly blazed out and attained a magnitude almost equal to that of the largest stars in the heavens. Huggins and Miller found that the spectrum of this star differed altogether from the ordinary stellar spectra, inasmuch as it was characterised by bright as well as by dark lines, and these bright lines were coincident with those of hydrogen. This shows that the star possessed a very singular physical constitution. The dark lines prove that it was to some extent constituted like our sun, whilst, in addition, a violent outburst

of incandescent hydrogen had taken place. As this star made its appearance suddenly, so it soon began to diminish in brilliancy, and at last returned to its original dimensions of about the tenth magnitude. A similar instance of the outbreak of a hitherto almost invisible star occurred in November, 1876, in the constellation of the Swan. It increased in brilliancy for a certain period, and then gradually diminished to its original magnitude. The spectrum of this star was exactly the same as that of T Coronæ.

SPECTRA OF THE NEBULÆ.

693 Astronomers have long attempted in vain to solve the question as to the nature of the nebulæ. By means of the spectroscope their nature has been, to a great extent, ascertained. Huggins finds that certain of the irresolvable nebulæ afford the same very distinct and remarkable spectrum. This consists of two or three bright lines lying in the green and blue portions of the spectrum. One of these lines is coincident with a line of hydrogen, whilst another corresponds exactly with a bright line of the nitrogen spectrum. Hence we may conclude with certainty that some of the nebulæ are composed of glowing gaseous matter, and consist, in all probability, of incandescent hydrogen and nitrogen gases, for although only one line of each of these elements has been observed, we know that under certain circumstances only one line in a spectrum is seen.

Spectra of Comets.—The examination of the spectra of comets is a subject of much interest. The nuclei of several comets have been examined spectroscopically.

These yield spectra consisting of bright lines, whilst the coma affords a continuous spectrum. Hence we may conclude that the coma shines by borrowed sun-light, but that the cometary nucleus is self-luminous.

MOTION OF THE FIXED STARS MEASURED BY SPECTRUM OBSERVATIONS.

694 The spectroscope likewise affords us information concerning the motions which the self-luminous heavenly bodies undergo with reference to the earth; and although this part

of the subject does not belong to chemistry proper, it is of such interest that the principles upon which it depends may be shortly mentioned. If a luminous particle is quickly approaching the eye of the observer, the wave-lengths of the rays it emits are diminished; whilst if the object is quickly receding a contrary action is noticed, and the wave-lengths are increased. Dr. Huggins by careful observations of the line F in Sirius has shown that the position of this line is shifted towards the red or that the wave-length has been increased by 0·109 millionth of a millimeter. The velocity of the consequent recession can be easily calculated. Light travels at 185,000 miles per second; the wave-length of the F line is 486·5 millionths of a millimeter. Now the velocity with which the two bodies move away from each other stands to the velocity of light in the same proportion as the observed difference of wave-length does to the wave-length of the particular ray; or—

$$486{\cdot}5 : 0{\cdot}109 :: 185{,}000 : x = 41{\cdot}4;$$

or the motion of recession between the Earth and Sirius was at that time 41·4 miles per second.

695 *Solar Cyclones.*—The same principle has been applied by Lockyer to determine the velocity of the solar cyclones. The red flames or prominences which are seen in a total eclipse to surround the sun, consist of incandescent hydrogen, calcium, and magnesium, with occasional irruptions of iron and sodium. The investigations of Janssen and Lockyer have shown that the changes in form and composition which these red flames undergo can now be observed in the sun's normal condition. These flames form a part of the incandescent solar atmosphere which surrounds the solid or liquid portions of the sun's body, rising to a height of 5,000 to 6,000 miles. From the displacement which the hydrogen line (F) exhibits, the velocity of up-rush or down-rush of the incandescent hydrogen can be ascertained. The velocity of these solar cyclones outstrips the most powerful imagination. In one case the velocity of ascent amounted to 166 miles per second.

The spectroscope likewise affords indications of the amount of pressure under which the incandescent gas exists in the solar atmosphere. The solar line F was noticed by Mr. Lockyer in many cases to be thickened out in the direction of the sun's surface like an arrow-head. This thickening out of the hydrogen line F can also be artificially produced in the laboratory by

reducing the pressure under which the gas is placed, and thus a means is opened out for ascertaining the pressure and possibly the temperature of the different layers of the solar atmosphere.

Again, Kirchhoff observed that sometimes one or more lines in a metallic spectrum appeared to be reversed in a solar spectrum, whilst the other lines did not suffer a reversal. Mr. Lockyer succeeded in explaining this singular fact, for he discovered that it is generally the *longest* lines of the metallic spectrum which are reversed in the solar atmosphere. These longest lines are seen in the spark-spectrum of the metal midway between the poles, whereas the shorter metallic lines are only noticed in the close proximity of the poles. Now it is probable that the vapour far removed from the poles is in a more rarefied condition than that close to the poles, so that the short lines are those which require for their existence a greater density of the vapour, and the long lines are those which can exist at a lower pressure. We are thus also led to the conclusion that it may be possible to ascertain the relative amounts of the several metallic vapours present in the solar atmosphere. In some cases all the lines are seen to be reversed, whilst in other instances only the long lines have their dark representatives in the solar spectrum.

THE NATURAL ARRANGEMENT OF THE ELEMENTS.

696 It has already been stated (vol. i. p. 80) that the chemical atom must rather be considered as a vibrating system of separate parts than as a physically indivisible whole. We are thus led to the idea that in process of time the so-called elementary bodies may be found capable of being decomposed into more simple components. Were this not the case, as many distinct kinds of matter must exist as we find different bodies as yet undecomposed, and this, for various reasons, is a very improbable supposition. We will at present mention only one of these reasons, viz., that the atomic weights of the elements exhibit, as has long been known, certain distinctive relationships.

So long ago as the year 1815, Prout[1] put forward the view that hydrogen, which possesses the smallest atomic weight of any element, is the only real elementary body, the atomic weights of all the other elements being supposed by Prout to be simple multiples of the atomic weight of hydrogen. The more exact determination of atomic weights subsequently made, especially by Berzelius, proved this theory to be erroneous. Dumas[2] many years later modified Prout's hypothesis, inasmuch as he assumed that the unit weight of hydrogen consists of two or even of four atoms, and that hence the atomic weights of the other elements must be regarded as multiples of 0·5 or 0·25. The careful quantitative investigations of Berzelius, Marignac, and especially those of Stas,[3] which latter were carried out with extreme care for the purpose of ascertaining the truth of Dumas's hypothesis, have however conclusively shown that the atomic weights of many elements are multiples neither of 1, nor of 0·5, nor of 0·25.

[1] Anonymously published in Thomson's *Annals of Philosophy*, vol. vi.: "On the Relations between the Specific Gravities of Bodies in their Gaseous State and the Weight of their Atoms."

[2] *Ann. Chim. Phys.* [3], lv. 129.

[3] *Nouvelles Recherches, &c.*

It is nevertheless remarkable that the atomic weights of many elements whose combining numbers have been accurately determined, approach very closely to whole numbers. Thus, for instance, we have :

Lithium	7·01
Nitrogen	14·01
Oxygen	15·96
Sodium	22·99
Sulphur	31·98
Potassium	39·04

On the other hand, certain elements possess atomic weights which are distinctly and considerably removed from the unit. Thus, for instance, we find :

Chlorine	35·37
Bromine	79·75
Iodine	126·53
Silver	107·66

These numbers, it is well to remember, are all of them accurate to within $\frac{1}{1000}$ of their amount, whilst some, such as chlorine and silver, are accurate to within $\frac{1}{10000}$ of the whole. In certain other elements the error attached to the atomic weight amounts to 1 per cent., whilst in a few cases the probable error reaches as high an amount as one-tenth of the total value.

697 Another important relationship which has long been known and which requires explanation, if Prout's hypothesis be not accepted, is the fact that in the case of groups of analogous elements the atomic weights frequently increase in the same ratio. As long as Prout's hypothesis was adopted it appeared reasonable to employ these relations between the atomic weights for the purpose of checking the atomic weights of those elements which had been less exactly determined, by means of those for which a more accurate determination existed. Thus, for instance, the following atomic weights were adopted :

	Difference.		Difference.
O = 16		Li = 7	
	16		16
S = 32		Na = 23	
	3 × 16		16
Se = 80		K = 39	
	3 × 16		
Te = 128			

It was assumed that these regular differences were to be explained by a common difference in the composition of the so-called atoms, similar to that observed in the homologous series of the carbon compounds, or rather in the compound radicals supposed to exist in these compounds; as, for instance, methyl, CH_3, ethyl, C_2H_5, propyl, C_3H_7, butyl, C_4H_9, &c. In this case, however, the difference between each member of the series and the next is a constant one, whilst in the case of the natural families of the elements this is not the case. At the same time the increase of the atomic weights is almost always either nearly a constant or some multiple of that constant, as is seen by reference to the following examples:

	Diff.		Diff.		Diff.		Diff.
N = 14·01		O = 15·96		F = 19·1		Na = 22·99	
	16·95		16·02		16·27		16·05
P = 30·96		S = 31·98		Cl = 35·37		K = 39·04	
	43·94		47·02		44·38		46·16
As = 74·9		Se = 79		Br = 79·75		Pb = 85·2	
	47·1		49		46·78		47·5
Sb = 122		Te = 128		I = 126·53		Cs = 132·7	

698 These singular relationships have been made the subject of inquiry and discussion on the part of many chemists. Thus, Lothar Meyer[1] in 1864 tabulated a large number of such groups and arranged a certain number of the elements in the order given in the above table, according, in the first place, to the magnitude of their atomic weights, and, in the second place, according to their atomicity.

It is, however, to Mendelejeff[2] that we owe a complete tabulation of the elements, even of those whose atomic weights were then uncertain. He proved that, in such a consecutive series, closely allied elements, or those which belong to one family, follow each other in regular periods. The whole series may thus be divided into groups, so that when the elements are placed under one another, each member of the group forms, with those lying alongside of it, a vertical series containing a natural family. The arrangement as first proposed by Mendelejeff contained many irregularities and many doubtful cases, which were gradually brought into harmony as the true atomic weights of these particular elements were ascertained.

[1] *Moderne Theorien der Chemie.* [2] *Zeitschr. Chem.*, 1869 405.

PERIODIC LAW OF THE ELEMENTS.

699 The first attempt to point out that the properties of the elements varied periodically was made by Newlands in 1863, but the statement did not at the time attract general attention, as a systematic arrangement of the elements according to their atomic weights appeared to some chemists to be almost as absurd as the proposal of an alphabetical arrangement of the elements as a natural one would be.[1]

The law of periodicity was afterwards further developed by Meyer[2] and Mendelejeff,[3] and thus a natural classification of the elements was shown to exist, which however is in some instances still somewhat arbitrary, inasmuch as even at the present time the atomic weight determinations of some of the elements are far from being exact. These relations are clearly exhibited in the table on page 507.

From this it is seen that the elements can be classed into eight chief groups, several of which are again divisible into sub-groups. The first chief group contains, in the first place, the metals of the alkalis, to which the copper group is attached by the isomorphism of some silver salts with those of sodium. These series also agree, inasmuch as they both form basic oxides having the composition M_2O.

The second chief group also consists of two sub-groups, (1) the metals of the magnesium group, and (2) those of the calcium group, several members of which are connected together by isomorphous relations.

In the third chief group we find the elements which form sesquioxides. The three last members are metals whose sulphates yield alums with the sulphates of the alkali metals, whilst connected with these we have the metals of the cerium group, of which there are probably several members yet to be discovered.

Next comes the group of the tetrad elements, which may probably be divided into two sub-groups.

Fifthly comes the characteristic nitrogen group, which is intimately connected with the sub-group of vanadium, niobium, and tantalum.

The sixth group is divided into two sub-groups, being con-

[1] *Chemical News*, vii. 70; x. 59; xxxii. 21, 129.
[2] *Ann. Chem. Pharm. Suppl.* vii. 354. [3] *Ibid.* viii. 133.

TABLE OF THE NATURAL ARRANGEMENT OF THE ELEMENTS.

I.			II.		III.				IV.	V.		VI.		VII.		VIII.		
Hydrogen 1	Lithium 7·01	—	Beryllium 9·2	—	Boron 11	—	—	—	Carbon 11·97	Nitrogen 14·01	—	Oxygen 15·96	—	Fluorine 19·1	—	—	—	—
—	Sodium 22·99	—	Magnesium 23·94	—	Aluminium 27·3	—	—	—	Silicon 28	Phosphorus 30·96	—	Sulphur 31·98	—	Chlorine 35·37	—	—	—	—
—	Potassium 39·04	—	—	Calcium 39·90	—	—	—	—	Titanium 48	—	Vanadium 51·2	—	Chromium 52·4	—	Manganese 54·8	Iron 55·9	Nickel 58·6	Cobalt 58·6
—	—	Copper 63·1	Zinc 64·9	—	Gallium 69·8	—	—	—	—	Arsenic 74·9	—	Selenium 79	—	Bromine 79·75	—	—	—	—
—	Rubidium 85·2	—	—	Strontium 87·2	—	Yttrium 89·6	—	—	Zirconium 90	—	Niobium 94	—	Molybdenum 95·6	—	Ruthenium 103·5	Rhodium 104·1	Palladium 106·2	—
	—	Silver 107·66	Cadmium 111·6	—	Indium 113·4	—	—	—	Tin 117·8	Antimony 122	—	Tellurium 128?	—	Iodine 126·53	—	—	—	—
—	Cæsium 133	—	—	Barium 136·8	—	Lanthanum 139	Cerium 141·2	Didymium 147	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	Erbium 169	—	—	Tantalum 182	—	Tungsten 184	—	Osmium 198·6?	Iridium 192·7	Gold 196·2	Platinum 196·7
—	—	Mercury 199·8	—	—	Thallium 203·6	—	—	—	Lead 206·4	Bismuth 210	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	Thorium 231·5	—	—	—	Uranium 240	—	—	—	—	—

nected by the isomorphous relations of the chromates and molybdates with many sulphates and selenates.

In the seventh group we find the chlorine family, with which manganese and ruthenium are closely connected owing to the isomorphism of the perchlorates, permanganates, and perruthenates; it is doubtful whether osmium ought to be classed in this group, although like the two other metals of its group it is readily oxidizable.

Lastly, in the eighth group, we have the iron family and the other members of the platinum group, which are closely related to the metals of the seventh group, by virtue of the analogy existing between the compounds of these metals and the cyanides of iron and the cobaltamine salts.

700 Many other analogies of the elements are exhibited by such an arrangement. Those which belong to different groups, but which formerly, owing to similarity in chemical and physical properties, were classed together, are found in the natural system in close proximity. Thus, for instance, lithium and magnesium, which both form difficultly soluble carbonates; and boron and silicon, which yield closely corresponding volatile fluorides as well as oxides which possess a certain analogy, are found not far removed from one another. Lead is also placed close to thallium; cadmium on the same line with indium and tin, and vanadium next to phosphorus. The vanadates exhibit a singular analogy with many chromates, and, for this reason, these elements were at one time classed together, just as tellurium was formerly considered to be closely connected with antimony.

These relations are still more strikingly exhibited if the table be rolled spirally round a cylinder, for in this way elements which are connected together by the isomorphism of many of their salts come close together; as, for example, the iron and copper group with the magnesium group, and the silver and mercury groups with the metals of the gold group.

Our table contains two exceptions marked with notes of interrogation. Tellurium stands before iodine, and osmium before the other metals of its group whose atomic weights are smaller. We do not at present know how these exceptions are to be explained; it may however be remarked that the atomic weights of all the members of the gold group require revision, as is proved by the result of the recent determination of the atomic weight of iridium.

Tellurium belongs most decidedly to the oxygen group, and in the same way ruthenium is closely connected with manganese. Osmium is, again, intimately allied to ruthenium, so that they must certainly be classed together.

701 Another glance at the table shows that matter becomes endowed with analogous properties when the atomic weight of an element is increased by the same or nearly the same number. Thus, starting from lithium, we find that its more important properties reappear in sodium, whose atomic weight is greater by sixteen, whilst another increment of about sixteen units brings us to potassium. If we add about forty-six to this, we then arrive at rubidium, and nearly the same increment again brings us to the atomic weight of cæsium. Similar relations are also observed in the case of other series, and hence we conclude that the *chemical properties of the elements are a periodic function of their atomic weights.*

The magnitude of the atomic weight in the several groups has a distinct influence on the chemical character of the elements. Thus, for instance, in groups three and four the lower members chiefly give rise to acids, whilst the higher members of the series yield basic oxides. On the other hand, elements which are placed in the centre, such as aluminium, yield oxides which act at the same time both as weak acids and bases. The special characteristic of the elements of groups six and seven is the formation of acids, which are the stronger the lower the atomic weight, whilst in the case of groups one and two the bases formed are more powerful the higher the atomic weight of the element is. We also find in other groups that the increase of the atomic weight is accompanied by increase in the acid-forming power of the oxides, or in the decrease of their basic properties.

702 The quantivalence or atomicity of the elements may also be regarded as a function of the atomic weight, and here the relation is even more clearly seen than it is in the case of the general chemical characters of the elements which we have already considered. Thus, for instance, the first members of each of the chief groups form the following compounds with either chlorine or hydrogen:

$$LiCl \quad BeCl_2 \quad BCl_3 \quad CH_4 \quad NH_3 \quad OH_2 \quad FH.$$

The quantivalence of the elements of these series gradually

rises from one to four, and then as gradually diminishes again. A similar phenomenon is observed in the other series, thus:

$$AgCl \quad CdCl_2 \quad InCl_3 \quad SnCl_4 \quad SbH_3 \quad TeH_2 \quad IH.$$

703 Other relationships also exhibiting a periodic variation with the atomic weight are observed when we compare the oxides, hydroxides, and hydrates. Or, inasmuch as the last series of compounds is very incompletely known, we may take their corresponding methyl compounds, or methides, which present close similarity to the hydrides:

Oxide.	Hydroxide.	Hydride.	Methide.
Na_2O	$NaOH$	—	$Na(CH_3)$
Mg_2O_2	$Mg(OH)_2$	—	$Mg(CH_3)_2$
Al_2O_3	$Al(OH)_3$	—	$Al(CH_3)_3$
Si_2O_4	$Si(OH)_4$	SiH_4	$Si(CH_3)_4$
P_2O_5	$PO(OH)_3$	PH_3	$P(CH_3)_3$
S_2O_6	$SO_2(OH)_2$	SH_2	$S(CH_3)_2$
Cl_2O_7	$ClO_3(OH)$	ClH	$Cl(CH_3)$

In order to render these relations more clearly visible, the above formulæ have been written, so as to show the correspondence in composition, without reference to their true molecular weights. Of these compounds chlorine heptoxide is not known, the corresponding perchloric acid only having been prepared. The probability that it can exist is however very considerable, inasmuch as we are acquainted with manganese heptoxide.

As may be seen from the above table, oxygen behaves in a totally different manner to hydrogen and the monad radicals; but the oxides, whether basic or acid-forming, stand in intimate relation to their hydroxides, and these again to their oxysalts.

The composition of the hydroxides depends, on the other hand, on that of their corresponding hydrides, inasmuch as the number of the hydroxyls which are replaced by oxygen in the oxide is equal to the number of hydrogen atoms in the hydride.

704 If we were to deduce, as some chemists are accustomed to do, the quantivalence of the elements from the composition of the above-named oxides, the elements of the nitrogen group must be considered as pentads, and the two following groups as hexads

and heptads. But the original idea of quantivalence (see vol. ii. part i., page 28) was deduced from the observation that different elements combine with 1, 2, 3, or 4 atoms of hydrogen to form volatile compounds, no compounds with 5, 6, or 7 atoms of hydrogen being known. In order to avoid confusion in this respect Lothar Meyer[1] has introduced the term *index of affinity*, by which he signifies the quantivalence obtained from the consideration of the composition of the highest oxides. He has shown that these, as well as their hydroxides, may be represented by the general formula

$$H_{2n}X_2O_{v+n} \text{ or } H_nXO_{\frac{v+n}{2}}$$

when (X) signifies the element in question, (v) the index of affinity, and (n) a small whole number. The compounds given on page 512 correspond, amongst others, to the above formula. Many of these formulæ are divisible by two, and the simple formulæ ordinarily in use are thus obtained. In a similar way the formulæ of the chlorates, sulphites, selenites, nitrites, and phosphites may be represented by the general formula

$$H_{2n}X_2O_{v+n-2},$$

and the chlorites, hypophosphites, and hyposulphites by the formula

$$H_{2n}X_2O_{v+n-4}, \text{ \&c.}$$

The oxychlorides and chlorides, &c., may be represented in a similar way, and thus a classification may be introduced corresponding to that which has long been employed in organic chemistry. Up to the present time, however, such an arrangement has been necessarily incomplete in the case of inorganic compounds, and one of the most important problems to the solution of which chemists have to direct their attention is the discovery of the general law which governs the relationships observed in the natural classification of the elements, for this law will express the mode of the formation of all chemical compounds.

[1] *Ber. Deutsch. Chem. Ges.* vi. 101.

	v = 1.	v = 2.	v = 3.	v = 4.	v = 5.	v = 6.	v = 7.
n = 0	K_2O Cu_2O	Mg_2O_2 Zn_2O_2	Be_2O_3 Al_2O_3	Si_2O_4 Ti_2O_4	P_2O_5 V_2O_5	S_2O_6 Cr_2O_6	Cl_2O_7 Mn_2O_7
n = 1	$H_2K_2O_2$ $H_2Cu_2O_2$		$H_2Al_2O_4$ (Diaspore) $MgAl_2O_4$ (Spinelle)	$H_2Si_2O_5$ (Opal)	$H_2P_2O_6$ $H_2V_2O_6$ $FeNb_2O_6$	$H_2S_2O_7$ $K_2Cr_2O_7$ $Na_2Mo_2O_7$	$H_2Cl_2O_8$ $K_2Mn_2O_8$
n = 2		$H_2Mg_2O_4$ $H_4Ca_2O_4$	$H_2Ag_2B_2O_5$	$Ca_2Si_2O_6$ (Wollastonite) Fe_2TiO_6 (Ilmenite)	$H_4P_2O_7$ $Ag_4V_2O_7$ $K_4Sb_2O_7$ $H_4Nb_2O_7$	$H_2K_2S_2O_8$ $K_4Cr_2O_8$ $Pb_2Mo_2O_8$ $Ca_2W_2O_8$	$K_4I_2O_9$
n = 3			$H_6B_2O_6$ $H_6Al_2O_6$	$H_4CaSi_2O_7$ (Okenite)	$H_6P_2O_8$ $Na_6V_2O_8$ $Ag_6As_2O_8$		$Pb_3I_2O_{10}$
n = 4				$Zn_4Si_2O_8$ (Willemite) $Be_4Si_2O_8$ (Phenacite)	$H_8Sb_2O_9$ (Volgerite)	$H_8S_2O_{10}$ $H_8W_2O_{10}$	$Zn_4I_2O_{11}$
n = 5						$H_8K_2Te_2O_{11}$	$Ag_{10}I_2O_{12}$ $H_{10}I_2O_{12}$

ATOMIC VOLUME AND ATOMIC WEIGHT.

705 Mendelejeff and Meyer have also shown that not only the chemical, but also the physical, properties of the elements stand in close relationship with their atomic weights, and that these properties also exhibit a close connection and periodic relation. Into this part of the subject we cannot, however, here enter, reserving it for the chapter on theoretical chemistry.

One point only we shall here mention, namely, the relationship which exists between atomic weight and atomic volume. By this last property we understand the number obtained by dividing the atomic weight by the specific gravity of the element. This undergoes a regular increase or diminution with variation of the atomic weight, as is shown in the following table, in which Mendelejeff's arrangement of the elements has been adopted for reasons which will be given later on:

Table of Atomic Volume-Relations.

Li=11·9 (0·59)	Be=4·4 (2·1)	B=4·1 (2·68)	C=3·6 (3·3)	N=?
Na=23·7 (0·97)	Mg=13·8 (1.74)	Al=10·7 (2·56)	Si=11·2 (2·49)	P=13·5) (2·3)
K=43·4 (0·86)	Ca=25·4 (1·57)	—?	Ti=?	V=9·3 (5·5)
Cu=7·2 (8·9)	Zn=9·1 (7·15)	—?	—?	As=13·2 (5·67)

The numbers in brackets are the specific gravities; the others are the atomic volumes.

CORRECTION OF DOUBTFUL ATOMIC WEIGHT.

706 Mendelejeff has pointed out that the periodic law may be employed for the correction of doubtful atomic weights, and also for predicting the probable existence and properties of elements which have hitherto not been recognised.

The following examples may serve to explain this important application of the law:

(1) The atomic weight of molybdenum is by some chemists assumed to be Mo = 96, whilst others take it in round numbers to be Mo = 92. The latter number does not fit into the natural system, inasmuch as in this case molybdenum would

be placed before niobium, and in the neighbourhood of elements with which it does not exhibit any analogies. The newer atomic weight determination of Liechti has confirmed these views, inasmuch as the true number appears to be 95·6.

(2) Uranium was formerly supposed to have an atomic weight of 60, and at a later period this number was doubled. The specific heat of this metal has not yet been determined, and neither of the above numbers fits into the natural system. In the first instance the metal would be placed between nickel and copper, and it does indeed show certain analogies with the metals of the iron group. But in order that the formulæ of its oxides might agree with those of the oxides of iron, uranium was taken to possess an atomic weight of 120; this alteration would place it between tin and antimony, metals with which it certainly has no analogies. Moreover, both the above-mentioned atomic weights are out of accord with the specific gravity of 18·4, which uranium is found to possess. The atomic weight of 240, which is now generally adopted, gives, however, to uranium a natural position in the chromium group.

ON THE EXISTENCE OF UNDISCOVERED ELEMENTS.

707 A cursory inspection of the last table shows the existence of three spaces in which no element occurs, and many more such spaces are noticed when all the elements are compared together in a similar way. According to Mendelejeff this is to be explained by the supposition that these spaces indicate the positions to be occupied by elements which have hitherto remained undiscovered; and he suggests that, in this way, it is possible to predict not only the existence, but even the properties of hitherto unrecognised elements. In order to avoid the introduction of a new nomenclature, Mendelejeff proposes to derive the names of the missing elements from the name of the first member of the series, prefixing, for the purpose of discrimination, the Sanscrit numbers *eka, diwi, tri, tschatur.* The three spaces in the foregoing table will, therefore, be filled up by the names *ekaboron, ekaluminium,* and *ekasilicon.* Respecting the second of these Mendelejeff says: "In its properties it stands between zinc and ekasilicon, on the one hand, and

between aluminium and indium on the other. Like the latter, it forms a sesquioxide; its atomic weight is about 68, its specific gravity about 6·0, and its atomic volume approaches 11·5." These predictions have been verified in the most remarkable manner. Ekaluminium turns out to be Lecoq de Boisbaudran's gallium, which has an atomic weight of 69·8, a specific gravity of 5·9, and an atomic volume of 11·8. Whether the other predictions will prove equally successful time alone can show.

The natural classification of the elements founded upon the relations exhibited by the atomic weights will, at some future period, form the starting-point for a true theory of chemical affinity. It will lead to the establishment of a system of inorganic chemistry corresponding to the much more complete system which now exists for organic compounds. Certain analogies thus become apparent which, without such a classification, might have been overlooked. Thus it could scarcely have otherwise happened that oxygen and chromium, chlorine and manganese, boron and indium, or sodium and copper, could be considered as analogous bodies belonging to the same natural groups. Much less probable does it appear that chemists should be able thus to predict not only the existence but even the physical and chemical properties of hitherto undiscovered elements.

ON THE CONDENSATION OF THE GASES FORMERLY CALLED PERMANENT.

708 In the first volume it is stated that Faraday endeavoured in vain to liquefy hydrogen, oxygen, nitrogen, nitric oxide, marsh-gas, and carbon monoxide. Natterer also obtained negative results in similar attempts, although in some of his experiments the above gases were subjected to a pressure of nearly 3,000 atmospheres. Andrews was also unsuccessful in this respect, although he not only employed a pressure which reduced the gases to $\frac{1}{300}$ part of their original volume, but also exposed them to the action of a low temperature. All the more remarkable, therefore, does it seem that towards the end of the year 1877 the public was informed that two experimenters almost simultaneously had succeeded in condensing the so-called permanent gases.

The meeting of the French Academy of the 24th December, 1877, was a memorable one. On that day the Academicians were told that Cailletet had succeeded in liquefying both oxygen and carbon monoxide at his works at Chatillon-sur-Seine, and that the former gas had also been liquefied by Raoul Pictet at Geneva.

These experimenters soon succeeded in condensing the other gases already named, and thus we are able to give experimental proof of the view which has been frequently expressed that all bodies without exception possess the power of cohesive attraction. These important results were arrived at independently by both observers, each having made the question the subject of many years' study and experiment. It is difficult, on reading the description of these experiments, to know which to admire most, the ingenious and well-adapted arrangement of the apparatus employed by Pictet, or the singular simplicity of that used by Cailletet. The latter gentleman is one of the greatest of French ironmasters, whilst the former is largely engaged as a

manufacturer of ice-making machinery, and the experience and practical knowledge gained by each in his own business have materially assisted to bring about one of the most interesting results in the annals of scientific discovery.

The process successfully adopted in each case consisted in simultaneously exposing the gas to a very high pressure and to a very low temperature. It has already been pointed out (vol. i. p. 79) that unless the temperature of the gas be lowered below the point termed by Andrews the critical point, no liquefaction of the gas can occur. In the case of oxygen, hydrogen, and the other gases formerly termed permanent, this critical point lies at a very low temperature, previously not reached by any experimenter; hence no amount of pressure applied to the gas above that point is sufficient to produce liquefaction.

The increase of pressure was effected by Pictet by evolving the gas in a wrought-iron vessel strong enough to withstand an enormous tension; whilst in Cailletet's arrangement the same end was brought about by a hydraulic press. For the purpose of obtaining a low temperature the first experimenter made use of the rapid evaporation of liquid carbon dioxide, thus producing a constant temperature of $-130°$. Cailletet, on the other hand, effected the same end by suddenly diminishing the pressure upon the compressed gas. This sudden expansion gives rise to a rapid diminution of temperature caused by the transference of heat into the motion of the particles of the expanding gas (*chaleur de detente*). So great is the amount of heat thus absorbed that the temperature of the particles sinks below the critical point of oxygen and hydrogen, and a condensation occurs, the finely divided liquid oxygen or hydrogen appearing as a mist in the tube.

LIQUEFACTION OF OXYGEN BY PICTET.

709 A vertical section and a ground plan of Pictet's [1] apparatus are shown in Figs. 192 and 193. p and p' are two pumps, p' being an exhausting, and p a compressing pump, such as are used in the ice-making machines. These are employed respectively for the volatilization and condensation of liquid sulphur dioxide, SO_2, contained in the outer inclined double-jacketed tube (R) Fig. 192; and both pumps are so arranged

[1] *Comp. Rend.* lxxxv. 1214, 1220; *Ann. Chim. Phys.* [5], xiii. 145.

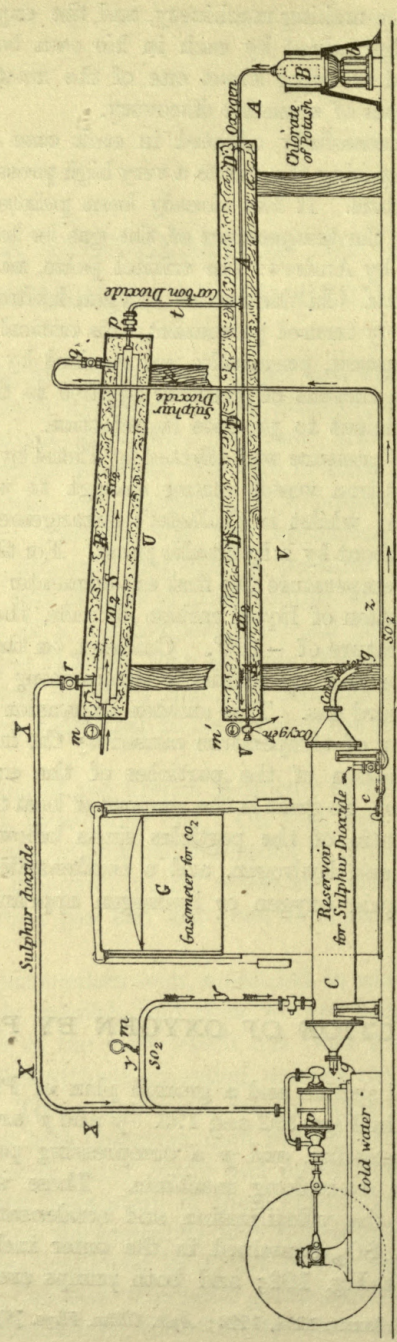

Oxygen
Chlorate of Potash
Carbon Dioxide
Sulphur Dioxide
Sulphur dioxide
Gasometer for CO_2
Reservoir for Sulphur-Dioxide
Cold water
Oxygen
SO_2

FIG. 192.

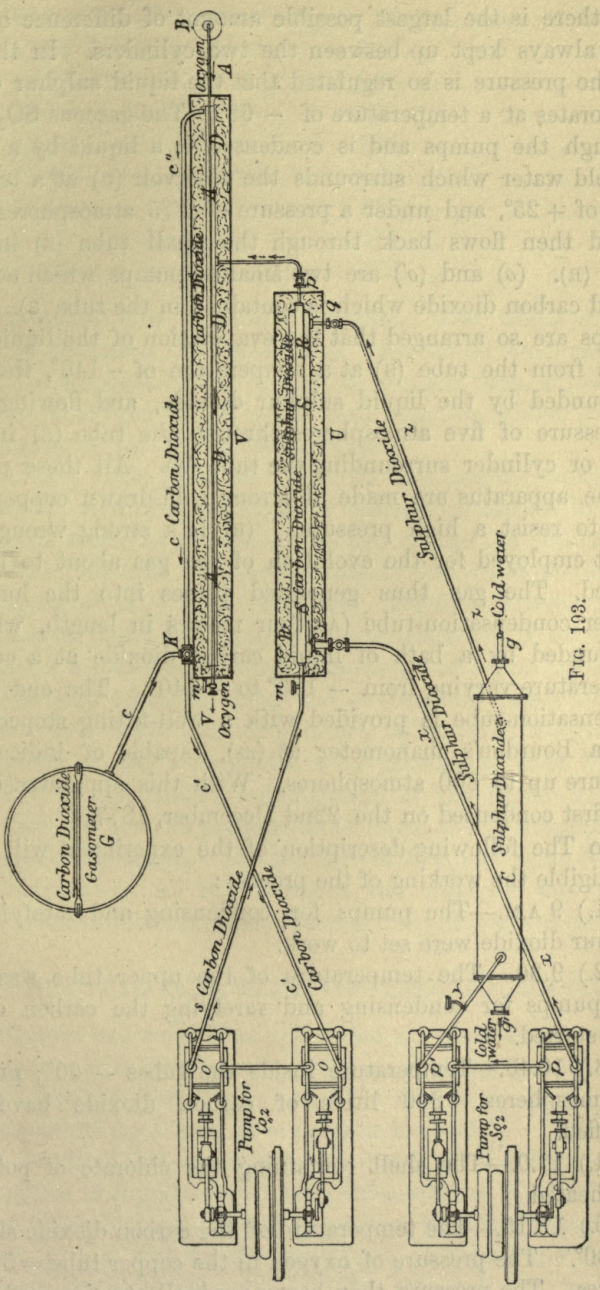

Carbon Dioxide Gasometer G
Pump for CO_2
Pump for SO_2
Cold water
Sulphur Dioxide
Carbon Dioxide
Oxygen

FIG. 193.

that there is the largest possible amount of difference of pressure always kept up between the two cylinders. In the tube (R) the pressure is so regulated that the liquid sulphur dioxide evaporates at a temperature of $-65°$. The gaseous SO_2 passes through the pumps and is condensed to a liquid by a stream of cold water which surrounds the reservoir (C) at a temperature of $+25°$, and under a pressure of 2·75 atmospheres. The liquid then flows back through the small tube (Z) into the tube (R). (*o*) and (*o'*) are two smaller pumps which act upon liquid carbon dioxide which is contained in the tube (S). These pumps are so arranged that the evaporation of the liquid takes place from the tube (S) at a temperature of $-140°$, this being surrounded by the liquid sulphur dioxide, and flowing under a pressure of five atmospheres through the tube (S) into the tube or cylinder surrounding the tube (A). All these portions of the apparatus are made of strong cold-drawn copper tubes able to resist a high pressure. (B) is a strong wrought-iron retort employed for the evolution of the gas about to be condensed. The gas thus generated passes into the long thin copper condensation-tube (A), four meters in length, which is surrounded by a bath of liquid carbon dioxide at a constant temperature varying from $-120°$ to $-140°$. The end of this condensation-tube is provided with a well-fitting stopcock (V) and a Bourdon's manometer at (*m*), capable of indicating a pressure up to 800 atmospheres. With this apparatus oxygen was first condensed on the 22nd December, 1877.

710 The following description of the experiment will render intelligible the working of the process:

(1.) 9 A.M.—The pumps for condensing and rarefying the sulphur dioxide were set to work.

(2.) 9.30.—The temperature of the upper tube was $-55°$. The pumps for condensing and rarefying the carbon dioxide were started.

(3.) 10.40.—Temperature inside the tubes $-60°$; pressure, 5 atmospheres. 800 litres of carbon dioxide have been liquefied.

(4.) 11.0.—The shell containing the chlorate of potash is now heated.

(5.) 11.15.—The temperature of the carbon dioxide sinks to $-130°$. The pressure of oxygen in the copper tube = 5 atmospheres. The pressure then began gradually to rise, and at last it remained constant, as is seen in the following table:

(6.) 12.10 P.M.—Pressure of oxygen 50 ats.; temp. as before.
(7.) 12.36 . . . . . 100 „ „
(8.) 12.37 . . . . . 200 „ „
(9.) 12.38 . . . . . 460 „ „
(10.) 12.40 . . . . . 525 „ „
(11.) 12.42 . . . . . 526 „ „
(12.) 12.44 . . . . . 525 „ „
(13.) 1.0 . . . . . 471 „ „
(14.) 1.5 . . . . . 475 „ „

The pressure now remained constant. The whole of the interior of the glass tube was filled with liquid oxygen. On opening the stopcock at the end of the oxygen tube, a lustrous jet of liquid oxygen issued with great violence, whilst around it was a haze of particles of solid oxygen.

On January 10th, 1878, M. Pictet, in like manner, succeeded in liquefying hydrogen obtained by heating potassium formate with caustic soda. At the end of the experiment the pressure in the condensation tube became constant at 650 atmospheres and at a temperature of – 140°. This may, therefore, be taken to be the tension of liquid hydrogen at that temperature. On opening the stopcock a *steel-blue* coloured opaque jet of liquid hydrogen rushed out with a hissing noise, and at the same time a rattling was heard as if small shot or hail had fallen on to the ground This appears to have been produced by particles of solid hydrogen formed by the sudden volatilization of the liquid striking the ground. When the pressure sank down to 370 atmospheres the stopcock was closed. It then fell to 320, and again rose to 325 atmospheres. At this moment the stopcock was again opened, and a similar continuous stream of hydrogen was emitted.

THE SPECIFIC GRAVITY OF LIQUID OXYGEN.

711 Dumas had some time ago stated on theoretical grounds that oxygen and sulphur must possess equal atomic volumes, and therefore that the specific gravity of the first in the liquid state of course would be 1, as that of sulphur is about 2. Pictet was able to confirm this prediction, inasmuch as he found that 45·467 grams of liquid oxygen occupied a volume of 46·25 cbc.

The general arrangement and appearance of Pictet's apparatus is shown in Fig. 194 on the next page, in which the end of the oxygen condensation-tube (A), the stopcock (V), and the manometer (*m*) are seen.

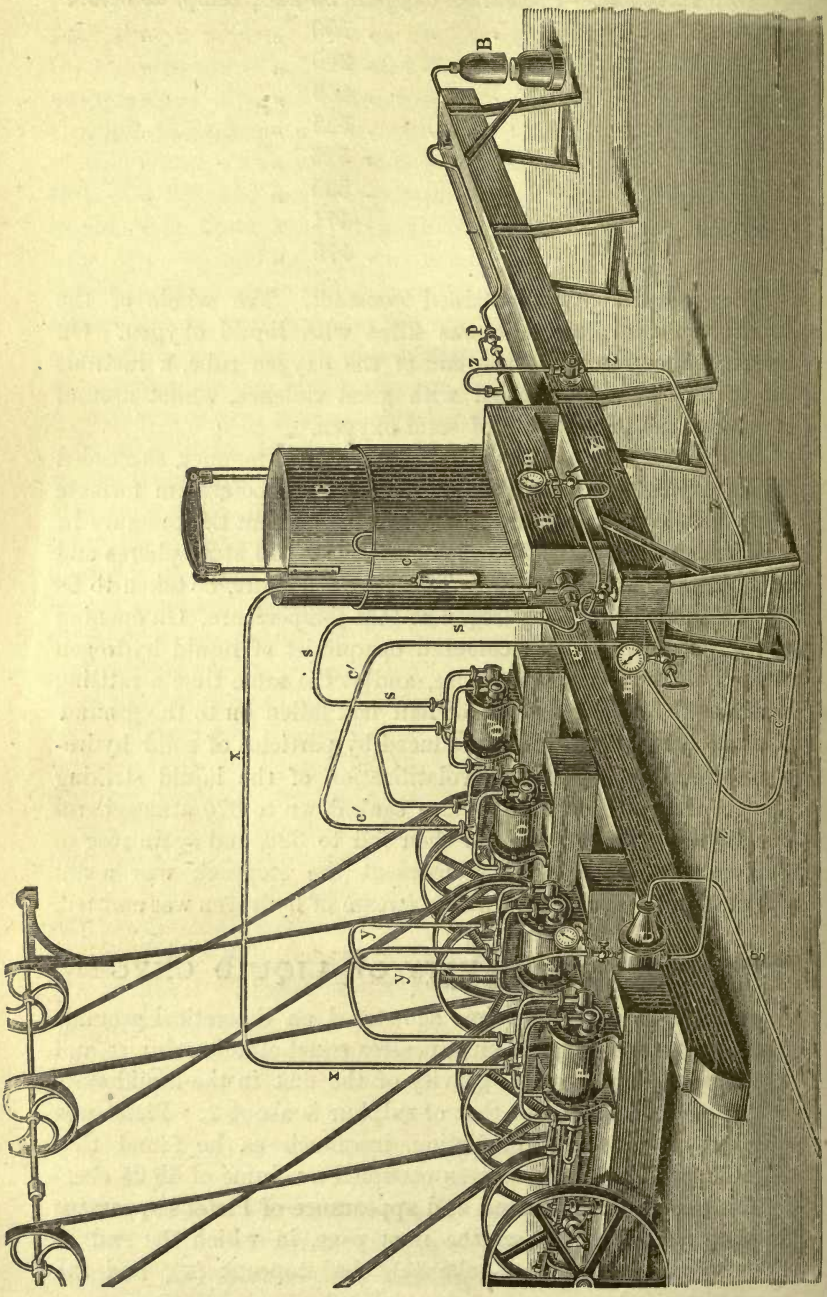


FIG. 194.

CAILLETET'S PROCESS FOR LIQUEFYING THE GASES.

The apparatus employed by M. Cailletet[1] for the liquefaction of oxygen and hydrogen is shown in Fig. 195. The first part of this apparatus consists of a powerful hydraulic press, the soft steel cylinder (A) of which is fixed by the bands (B B) on to a horizontal cast-iron bed. A steel piston works into this cylinder through a stuffing-box, and to the end of the piston is attached the screw (F), which can be carried backwards or forwards by turning the wheel (M) either in one direction or the other. The hydraulic cylinder is filled with water from the vessel (G), and this communicates with the interior of the cylinder by a fine opening, which can be perfectly closed at pleasure by means of a conical valve attached to a piston worked by the wheel (O). On withdrawing this piston water flows into the cylinder.

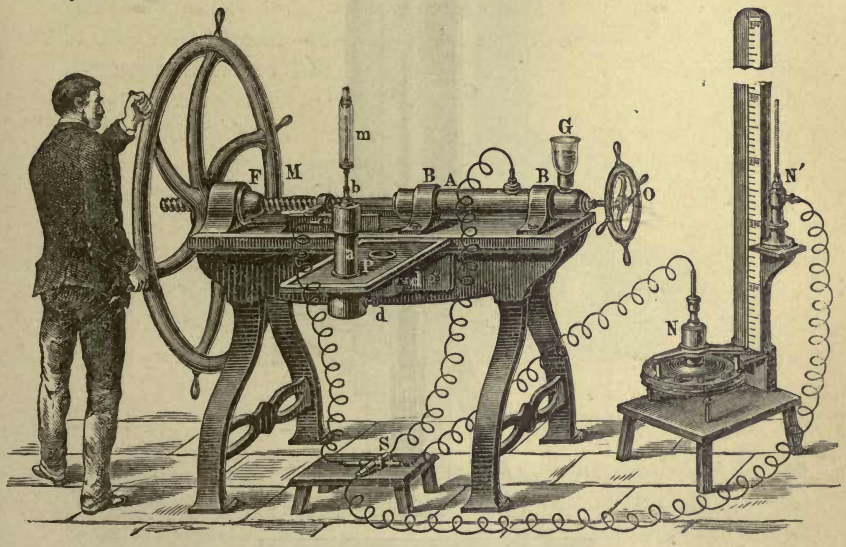


FIG. 195.

The second part of the apparatus is the receiver (Fig. 197). This consists of a glass tube with reservoir at the lower end firmly bedded into a steel head (B, Fig. 197), sufficiently strong to resist a pressure of 1,000 atmospheres. This receiver is placed

[1] *Compt. Rendus*, x. 85, 815; and *Ann. Chim. Phys.* [5], 15, 132.

in direct connection with the hydraulic pump by means of a flexible metallic tube (TU) of small diameter. A steel head is firmly screwed on to the upper part of the receiver by the screw (E′), and this head carries the glass tube (T), which contains

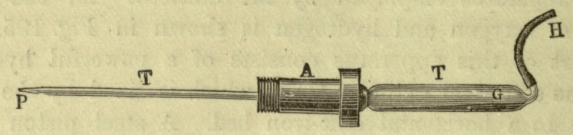


FIG. 196.

the gas to be experimented upon. The shape and mode of fixing this tube with its reservoir of gas is seen in Fig. 196; whilst in Fig. 197 the same is shown placed in position with the lower portion dipping into the mercury which fills the lower

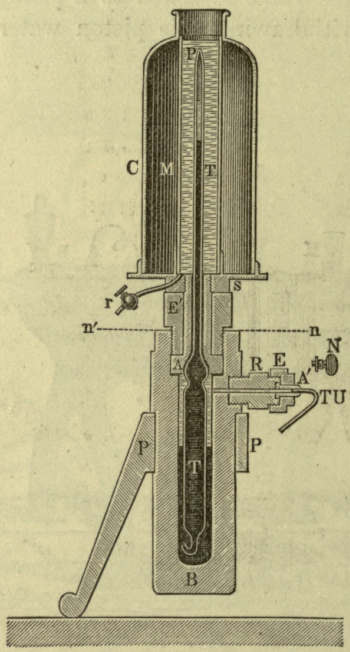


FIG. 197.

part of the steel receiver. As the glass reservoir is exposed to the same pressure on both its inside and outside surfaces, its dimensions may be made large in spite of the extremely high pressures to which it is subjected in the course of the

experiments. The thin tube, on the other hand, which passes out above the steel head of the condenser has of course to support the pressure necessary for the condensation of the gases, and hence it must be made of strong glass with a capillary bore. A glass cylinder (M) resting on the iron flange (S) serves to enable the experimenter to surround the tube either with a freezing-mixture or with a warm liquid. When the reservoir has been filled with the pure dry gas under examination the end of the tube is carefully hermetically sealed, and the whole screwed into position. Water is then forced into the receiver from the hydraulic cylinder; this forces the mercury into the reservoir, and the

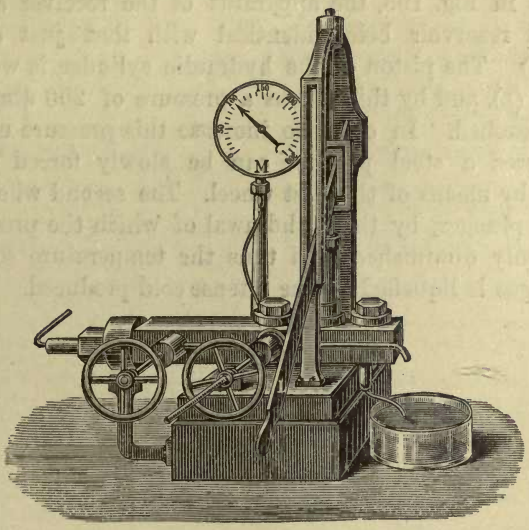


FIG. 198.

compressed gas condenses in the capillary tube, where the changes which occur can be readily observed. The position of the receiver and capillary tube is shown at *a* and *m* Fig. 195. The pressure is measured by two manometers (N and N′, Fig. 195.

With this apparatus Cailletet liquefied ethylene at +4° under a pressure of 46 atmospheres; acetylene under the ordinary temperature at a pressure of 86 atmospheres; nitric oxide and marsh gas required to be cooled to −11°, and these became liquid at the respective pressures of 104 and 108 atmospheres. Oxygen and carbon monoxide remained liquid at a temperature

of $-29°$ under a pressure of 300 atmospheres. When, however, this pressure was suddenly reduced a thick mist was formed in the tubes, and this condensed, forming small drops of nitrogen at a temperature of 13 and under a pressure of 200 atmospheres. Hydrogen, on the other hand, appeared, when the pressure from 300 atmospheres was suddenly removed, in the form of a slight mist, but dried air liquefied under a pressure of 200 atmospheres after it had been well cooled with liquid nitrous oxide.

712 An apparatus for exhibiting the liquefaction of the difficultly condensible gases has been constructed by Messrs. Ducretet et Cie of Paris.[1] The condensing arrangements of this apparatus are seen in Fig. 198, the apparatus of the receiver and glass tube and reservoir being identical with that just described (Fig. 197). The piston of the hydraulic cylinder is worked by the lever (L), and by this means a pressure of 200 atmospheres can be reached. In order to increase this pressure up to 300 atmospheres a steel plunger can be slowly forced into the cylinder by means of the first wheel. The second wheel works a second plunger, by the withdrawal of which the pressure can be suddenly diminished, and thus the temperature so reduced that the gas is liquefied by the intense cold produced.

[1] Rue des Feuillantines, 89.

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**** *The Second Volume has been published in Two Parts, separately paged. This Index embraces the Two Parts, and the Roman Numerals* (i. ii.) *refer respectively to the Pages of the* First *and* Second *Parts of the Volume.*

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